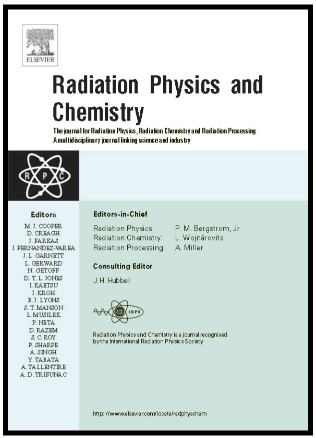

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Mass spectrometric comparison of swift heavy ion-induced and anaerobic thermal degradation of polymers

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Abstract

The study of polymers irradiated by highly energetic ions and the resulting radiation-induced degradation is of major importance for space and particle accelerator applications. The mechanism of ion-induced molecular fragmentation of polyethylene, polyethyleneimine and polyamide was investigated by means of mass spectrometry and infrared spectroscopy. The results show that the introduction of nitrogen and oxygen into the polymer influences the stability rendering aliphatic polymers with heteroatoms less stable. A comparison to thermal decomposition data from literature reveals that ion-induced degradation is different in its bond fracture mechanism. While thermal degradation starts at the weakest bond, which is usually the carbon-heteroatom bond, energetic ion irradiation leads in the first step to scission of all types of bonds creating smaller molecular fragments. This is due to the localized extreme energy input under non-equilibrium conditions when the ions transfer kinetic energy onto electrons. These findings are of relevance for the choice of polymers for long-term application in both space and accelerator facilities.

Keywords:
Polymer degradation, heavy ion irradiation, radiation damage, thermal polymer degradation

Highlights:
-Particle accelerator experiments give information about aliphatic polymer degradation.
-High energy ions irradiation simulates use in space and accelerator application.
-Small molecule fragments are the dominant product.
-Single-bonded heteroatoms like nitrogen and oxygen introduce predefined scission points.
-Ion-induced degradation shows a different behavior than thermal decomposition.

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1. Introduction

Insulators used in space in satellites, telescopes and vehicles are exposed to all kinds of radiation, including highly energetic particles of Galactic Cosmic Rays [1]. Accelerator facilities and nuclear power plants demand the same requirements on insulators, considering their high radiation environments. The new *Facility for Antiproton and Ion Research* (FAIR) which is presently under construction at the *GSI Helmholtzzentrum für Schwerionenforschung* in Darmstadt, Germany, is designed to deliver beams of radioactive and stable heavy particles up to uranium ions with intensities as high as 10^{12} ions s^{-1} and energies up to 20 GeV per nucleon [2]. During beam operation, devices such as the superconducting magnets will be exposed to high-dose radiation of X-rays, gammas, neutrons, and to some extent to charged particles, including ions of low to medium mass. Radiation-induced degradation in organic materials depends primarily on the absorbed dose, but also on the type of radiation. The type can differ in penetration depth, intensity, and spatial energy deposition as well as environmental factors such as temperature and atmosphere [3]. The radiation field around accelerators is predominantly composed of light particles, such as neutrons and protons. However, even heavier elements, such as carbon, can be found. The latter are generated from primary particles which fragment when they hit the beam line tubes. This leads to a significant interest in the influence of particle radiation on insulation materials. Ceramics and polymers are the most common materials used as insulators for superconducting magnets. Ceramics that are known to have the advantage of a higher radiation hardness compared to polymers might seem to be the better choice. However, beam conducting magnet superconductors operate at room and low temperatures, which increases the importance of the difference of thermal expansion coefficients in construction materials significantly [4]. Due to a very low ductility and a brittle structure of ceramic materials, the slightest variance in thermal expansion coefficients compared to the conducting material might cause ruptures/structural damage in the superconducting magnet insulation. Though polymers can be used in the harshest environments for insulation purposes and do not suffer from problems with expansion upon cooling, they are rather prone to highly energetic radiation. Therefore, it is of interest to study their stability against particle radiation.

The general effects of irradiation with ion beams of MeV-GeV kinetic energy on polymers are well documented in literature, e.g. [5,6,7]. Modification of aliphatic polymers through swift heavy ions has been investigated by several groups, e.g. by Balanzat et al. [7,8] on polyethylene (PE) and polystyrene (PS), or on polymethyl methacrylate (PMMA) [5] and different polyvinyls (PVA, PVAc, PVF) [6]. The interaction of energetic ion beams with polyimide (Kapton™) has been studied by several groups, investigating radiation-induced degradation and damage track formation by means of spectroscopy (e.g. IR, UV-Vis, Raman), high-resolution microscopy (e.g. scanning force and transmission electron microscopy) and other techniques [3,9]. However, there is still a lack of knowledge regarding the radiation hardness of particular polymers under irradiation with heavy ions, especially in terms of their molecular degradation mechanism.

In general, each ion produces a track of structurally changed bulk material along its trajectory, whose core is typically a few nm in diameter and surrounded by a cylindrical halo-like degraded area. This zone shows known changes of morphological characteristics [10]. This enables a modification of any polymer film beyond the surface into the bulk material [11]. It can even induce the creation of alkynes, which was revealed through studies by means of infrared (IR) spectroscopy and is not observed in classical radiation experiments [12].

In this study, we concentrate on radiation-induced degradation effects of three types of polymers. Polyethylene (PE), polyethyleneimine (PEI), and polyamide (PA6) were exposed to highly energetic heavy ions, simulating harshest radiation environment and providing estimates of the performance under the worst case scenario. PE is the simplest polymer, homogeneously structured and consisting only of carbon and hydrogen (see Fig. 1a). It is commonly used in many applications, either as high density Polyethylene (HDPE), linear low density polyethylene (LLDPE) or low density polyethylene (LDPE). Typical applications are electrical insulation and packaging. The structure of PEI is similar to PE, containing nitrogen as an additional heteroatom (Fig. 1b), whereas PA6 introduces the amide group, containing nitrogen and oxygen as additional heteroatoms (Fig. 1c). PEI is used in detergents, adhesives, water treatment agents and cosmetics. PA6 was chosen to evaluate the difference, when a more complex functional group is introduced to the carbon-hydrogen-backbone. PA is used as fibres, in car components and food packaging.

It is necessary to compare the degradation behavior of the polymers and understand the role of the different elements and bond types. The degradation was compared to anaerobic thermal decomposition of the polymers, to evaluate the effect of irradiation under non-equilibrium conditions.

Those three polymers were chosen due to their increasing complexity building up on each other. Whereas PE is a simple hydrocarbon polymer, PEI already has nitrogen as a heteroatom in the repetition sequence. In the case of PA the amide group with an oxygen as a further element is introduced. Hence, it is helpful to analyze the similarities and differences during irradiation experiments to enable the design of insulating polymers with increased radiation hardness. In addition, the experimental data on radiation-induced decay presented here are of special concern for the superconducting magnets of the ion synchrotron SIS100 of the FAIR facilities.

2. Experimental

2.1 Materials and irradiation

Commercial-type foils of PE and PA6 were purchased from Goodfellow, providing a thickness of 20 µm. The polymer foils were, prior to irradiation experiments, cut to squares, with a side length of 2.5 cm. These samples were irradiated under high vacuum with $^{197}Au^{25+}$ ions with an energy of 11.1 MeV/u, corresponding to a total kinetic energy of ca. 2.2 GeV, at the universal linear accelerator (UNILAC) of GSI *Helmholtzzentrum für Schwerionenforschung*. The experimental setup with sample chamber and in situ spectroscopy has been described elsewhere [13]. The PEI foils were produced with a saturated solution of PEI (Polysciences) in Dichloromethane, which was spread out by using a squeegee to a thickness of about 20 µm and dried. The PEI samples were irradiated with $^{48}Ti^{11+}$ ions with an energy of 0.5 GeV. The applied particle fluences were increased from $1x10^{10}$ up to $2x10^{12}$ ions cm^{-2} with the beam flux limited to $2x10^{8}$ ions $cm^{-2}s^{-1}$ to avoid sample heating. The fluence was measured by monitoring the signal from a secondary-electron emitting Al-foil-detector placed in front of the samples and calibrated via a Faraday cup (precision ~ 20%).

2.2 Infrared spectroscopy

After irradiation, the 20 µm thick polymer foils were characterized by Fourier transform infrared (FTIR) spectroscopy. The FTIR measurements were performed by a Nicolet Magna-IR 550 spectrometer (spectral resolution of 2 cm^{-1}) in the transmission mode. The IR beam was adjusted in a line through the vacuum chamber with the sample holder with two IR-transparent vacuum windows [13]. Before each irradiation experiment, a spectrum of the pristine polymer was recorded. After the irradiation step, the modified material was measured

under identical conditions. The background of the spectra was subtracted, then the difference spectra were calculated. Thus, the structural effect of ion irradiation became visible.
The absorption bands were analyzed with the baseline method determining the absorbance of the centroid peak height. The spectra were recorded under the Brewster angle of 55° to avoid interference effects.

2.3 Mass spectrometry (Residual Gas Analysis)
The residual gas in the irradiation chamber was monitored with a quadrupole mass spectrometer from Balzers (Prisma QMS 200), operated in the single ion mode for a mass-to-charge ratio (m/z) from 1 to 100. The head of the QMS was positioned close to the sample, outside of the beam trajectory. Prior to irradiation of the polymer foils, background measurements of the chamber were recorded without and with beam on the empty sample holder. During all experiments, the chamber was evacuated with a turbomolecular pump (10^{-5}–10^{-4} Pa). A typical measuring cycle consisted of monitoring the QMS signal during irradiation of the 20 µm thick polymer foil, while measuring the outgassing compounds simultaneously.
After reaching a fluence of $1.5x10^{12}$ ions cm^{-2}, the samples were visually inspected for fissures.

3. Results

As mentioned before, for this study three polymers have been compared, to evaluate molecular/structural influences on radiation stability. Radiation-induced changes can be monitored by IR spectroscopy as well as by mass spectrometry when ion-induced fragmentation is investigated.

3.1 Infrared spectroscopy
IR spectroscopy is a useful method to monitor the degradation of functional groups of the polymer chains *in-situ*. The peaks were assigned according to known literature [14].

In Fig. 2 IR spectra of irradiated and unirradiated PE multiplett peaks at 2800 cm^{-1} are depicted, showing the presence of carbon-hydrogen-bonds through their stretch vibrations, and sharper peaks at 1500 cm^{-1} for bending and 725 cm^{-1} for rocking vibrations of carbon-hydrogen bonds. In case of irradiated PE the infrared spectrum shows the peaks of all alkane carbons-hydrogen bonds diminishing (Fig. 2, green graph). This is a clear indication that PE degrades, as C-H-bonds are broken. The interesting transformation of the carbon-hydrogen-bond vibration at 1470 cm^{-1} (Table 1) might be a consequence of hydrogen loss and new available degrees of freedom. The formation of carbon-carbon double bonds in the backbone is implicated through a weak appearance of a peak at 650 cm^{-1}. The corresponding stretch vibrations signal of the carbon-carbon double bond, which should be between 3100 cm^{-1} and 3000 cm^{-1}, might be shifted in the multiplett at 3000-2850 cm^{-1}.

Table 1. Overview of bond vibrations at certain wavenumbers, which match to PE IR spectra.

Bond vibration (functional group)	**Wavenumber (absorption)/cm^{-1}**
C-H stretch	3000-2850 (m)
C-H bend	1470-1450 (m)
C-H rock	725-720 (m)
C=C-H bend	680-500 (m)

The IR spectra of PEI (Fig. 3.) show significant signals of carbon-hydrogen bond vibrations between 720 cm^{-1} and 1500 cm^{-1}, as well as vibrations of carbon-nitrogen bonds at 1600 cm^{-1} and a weak band at 3490 cm^{-1}. The most significant decrease in peak intensity due to ion irradiation is observed for the carbon-hydrogen rocking vibration at 725 cm^{-1}. All other carbon-hydrogen bond vibrations decrease similarly. Though the nitrogen-hydrogen bond vibration at 1600 cm^{-1} (see Table 2) decreases significantly equivalent to the carbon-hydrogen-bond vibrations, the diminishing of the nitrogen-hydrogen-stretch vibration at 3490 cm^{-1} (see Fig. 3.) is less pronounced and indicates a slower decrease of the amount of terminal amines. Instead, a stretch vibration at 2250 cm^{-1} (see Table 2) is observed to appear, whereas the carbon-nitrogen-stretch vibration at 1150 cm^{-1} degrades. This indicates a cleavage of a C-N-bond and loss of the secondary amino group and possible conversion into a nitrile.

Table 2. Overview of bond vibrations at certain wavenumbers, which matches for PEI IR spectra.

Bond vibration (functional group)	**wavenumber (absorption)/cm^{-1}**
N-H stretch (1° amine)	3400-3250 (m)
C-H stretch (alkane)	3000-2850 (m)
C=N stretch (nitrile)	2250-2210 (m)
N-H bend (1° amine)	1650-1580 (m)
C-H bend (alkane)	1470-1450 (m)
C-H rock (alkane)	1370-1350 (m)
C-N stretch (aliphatic amine)	1250-1020 (s)
C-H rock (alkane)	725-720 (m)

The irradiation of PA6 shows a decrease of peaks at 3400 cm^{-1} in the spectra, belonging to primary amines (see Fig. 4). There is a significant increase of carbonyles, especially aldehydes at 1740 cm^{-1}, combined with a decrease of ketones. In comparison, the vibration of the carbon-hydrogen bond at 2900 cm^{-1} (Table 3) seems not to be much affected. The infrared spectrum (Fig. 4) even indicates a decrease of secondary amines at 750 cm^{-1} in the backbone, which might transform into vibration signals of primary amines at 3400 cm^{-1}.

Table 3. Overview of bond vibrations at certain wavenumbers, which matches for PA-IR spectra.

Bond vibrations (functional group)	**Wavenumber (absorption)/cm^{-1}**
O-H stretch (alcohol)	3400-3200 (m)
N-H stretch (1° amide)	3400-3250 (m)
C-H stretch (alkane)	3000-2850 (m)
C=N stretch (nitrile)	2260-2210 (m)
C=O stretch (carbonyle)	1760-1665 (s)
C=O stretch (aldehyde, saturated aliphatic)	1740-1720 (s)
C=O stretch (aldehyde, unsaturated aliphatic)	1710-1665 (s)
C=C stretch (alkene)	1680-1640 (m)
C-H bend (alkane)	1470-1450 (m)
C-H rock (alkane)	1370-1350 (m)
C-N stretch (aliphatic amine)	1250-1020 (m)
N-H wag (2° amine)	910-665 (s)
C-H rock (alkane)	725-720 (m)

The carbon-carbon bonds showed the least degradation followed by carbon-oxygen bonds. The highest decrease in absorption was found for carbon-nitrogen bonds. This seems to correlate with the dissociation energies of the above mentioned bonds. The comparison of the three polymers suggests a decreasing radiation hardness from PE to PA6 to PEI, as the introduction of heteroatoms seems to weaken the polymer backbone. To gather more information about the degradation process mass spectrometry measurements were conducted.

3.2 Mass spectrometry

All polymers were further characterized by residual gas analysis (RGA), i.e. quadrupole-based mass spectrometry (QMS), during irradiation. Prior to ion irradiation, vacuum background measurements were carried out. For comparison to thermal decomposition, known mass fragments from literature where included in the tables. All mass spectra show characteristic peaks corresponding to the outgassing species of the polymer itself but also peaks derived from desorbed gas of the vacuum chamber wall and gas leakages.

The mass spectrometric signal m/z = 2 (see Tables 4, 5 and 6) indicates the presence of hydrogen molecules as the most prolific volatile species and m/z = 18 indicates the presence of water.

Table 4. Mass fragments detected during irradiation of PE in comparison to thermal degradation from the literature (”-“ means minor signal or no fragment).

Mass peaks	**Fragments by ion irradiation**	**Fragments by thermal decomposition [15]**
2	H_2	-
12	C^+	-
13-16	CH_x^+	CH_x^+
18	H_2O^+ (backgrd.)	-
26	$C_2H_2^+$	-
26-30	$C_2H_x^+$	$C_2H_x^+$
38-44	$C_3H_x^+$	$C_3H_x^+$
>50	-	$C_4H_x^+$
>65	-	$C_5H_x^+$
>80	-	$C_6H_x^+$
>98	-	$C_7H_x^+$

For the analysis of PE, next to the large hydrogen and the water peaks, a large peak appears at m/z = 26, assigned to ethyne C_2H_2. It is accompanied by the peaks of further hydrocarbons, based on 2 C atoms, but with different numbers of hydrogen atoms. At lower mass numbers, methane and its H-depleted fragments can be found. Among the series m/z 38-44, deriving from scission of the polymer chain and the resulting short hydrocarbons $C_3H_{x,}$ the mass signal m/z = 42, most probably H-depleted propane radical or propene, exhibits a large intensity (see Table 4). The degradation scheme (see Fig. 6) illustrates that the broken bonds, either carbon-hydrogen or carbon-carbon, result in various charged fragments of the polymer. The decrease of mass signals above 60 implies that the formation of larger polymer fragments is less probable or they are not able to leave the bulk polymer as easily as the smaller ones along the ion tracks. Smaller hydrocarbon fragments are more mobile than longer chain fragments.
In contrast to ion-induced fragmentation, for thermal decomposition in literature mainly larger chain fragments including olefins were found [15]. The reason for the difference of thermal decomposition to ion-induced decomposition is supposed to be based on the kind of energy input. In the thermal case there is a uniform energy level. After chain scission, the fragments can further undergo reactions and transform into energetically more stable states. In contrast, in ion irradiation, the energy input is massive and highly localized along the ion tracks. Small molecular fragments have the chance to leave the material in a short time along paths that allow for ion enhanced diffusion.

Table 5. Mass fragments detected during irradiation of PEI in comparison to thermal degradation from the literature.

Mass peaks	Fragments by ion irradiation	Fragments by thermal decomposition [16,17]
2	H_2	-
14	N^+, CH_2^+	-
16	NH_2^+, CH_4	
17	NH_3^+/OH^+	NH_3^+
18	H_2O^+	-
26	CN^+, $C_2H_2^+$	-
28	CH_2N^+, $C_2H_4^+$, (N_2^+)	-
30	-	CNH_4^+
42	$C_2H_6N^+$	$C_2H_6N^+$
76	-	C_4H_5N
95	-	C_6H_4N

In analogy to PE, the mass spectrum of PEI also contains a large hydrogen and water signal. The masses detected are different, since the polymer contains nitrogen. In contrast to the mass spectrum of PE, a large signal appears at m/z = 28. This larger mass is assumed to be due to the presence of nitrogen. The mass can be assigned to a carbon-nitrogen fragment, to a carbon-hydrogen-fragment and, less probable, to molecular nitrogen (see Table 5).

In the thermal degradation process mostly different volatile fragments are found. Again, these are heavier than the ones in the ion beam case [16, 17]. Thermal decomposition of PEI takes place at 230°C and the lowest masses except for ammonia, are found at m/z = 30 and at m/z = 42 [16].

The scission of bonds in the backbone chain may induce the formation of nitrile groups in the polymer chain (Fig. 8). An increase of cumulative nitrile groups could also lead to alkenes or even alkynes if the connecting carbon-carbon bond is cleaved through irradiation, as indicated in the IR spectra. The fragments indicate, that the carbon-nitrogen bond is both less irradiation resistant and thermal resistant than the other bonds of the polymer.

Table 6. Mass fragments detected during irradiation of PA6 in comparison to thermal degradation from the literature.

Mass peak	**Fragments by ion irradiation**	**Fragments by thermal decomposition [18,19]**
2	H_2	-
12	C^+	-
14	CH_2^+, N^+	-
15	-	NH^+
16	O^+	-
17	NH_3^+/OH^+	
18	H_2O^+	H_2O^+
25	C_2H^+	
26	$CN^+/C_2H_2^+$	
27	HCN^+	HCN
28	CO^+, CH_2N^+, $C_2H_4^+$,	-
29	CH_3N^+	-
30	-	C_2H_4
32	O_2^+	-
41	-	$C_3H_5^+$, $C_2H_3N^+$
44	CH_2NO^+, CO_2	CO_2
55, 56	-	fragments of $C_6H_{11}NO$
84, 85	-	fragments of $C_6H_{11}NO$
113	-	$C_6H_{11}NO$

For PA6, apart from the water peak, the largest peak in the spectra appears at m/z = 28. In contrast to PEI, next to CH_2N^+ and $C_2H_4^+$, the fragment is most likely carbon monoxide (CO) (see Table 6). This occurrence of CO is not described in literature on thermal decomposition. In contrast, in thermal decomposition carbon dioxide (CO_2) is present. The weakly pronounced mass peak at m/z = 44 could be attributed to $CO_{2,}$ but also to an amide. The suggested scheme of degradation through particle irradiation (see Fig. 10) shows bond scission at oxygen (see Fig. 10) or nitrogen (see Fig. 10) leading to the formation of methane amide. In contrast to thermal degradation, where caprolactam and different fragments of it were found [18, 19], no significant volumes of higher mass fragments are observed under irradiation.

In general, in the ion irradiation experiments mainly small mass fragments where found. The polymers show a pronounced sensitivity towards heavy ion irradiation. The localized large energy input leads to multiple fragmentations and bond scissions in close distances, thus producing small molecular fragments.
However, it has to be considered that the vacuum environment supports the elimination of small fragments from the polymer. These are more mobile and volatile than larger ones. Whether their large quantity could furthermore mask any small amounts of larger fragments in the detector is not clear.

4. Discussion

PE irradiation shows that the carbon-hydrogen bonds, despite being among the strongest in organic chemistry, are very sensitive to swift heavy ions, as all organic matter. When introducing heteroatoms into the polymer, such as nitrogen in PEI and nitrogen and oxygen in PA6, the heteroatoms seem to facilitate the cleaving of the polymer at the backbone. This might be due to their capability of stabilizing radical electrons better than saturated alkane-like structures.

The appearance of mainly small molecular fragments of PE in the mass spectrum upon ion irradiation can be attributed to two effects: One is that the ion beam cuts the polymer to small fragments due to extreme energy and forces introduced in small volumes around the ion track. The second one could be due to the less volatile nature of larger polymer chain fragments at room temperature (RT). Even an already several times cleaved polymer chain might show enough entanglement in the bulk material to stay in place. With more scission, the smaller fragments become volatile and can be detected.

The difference to thermal decomposition is that the latter does hardly show small fragments. Under ion irradiation, the polymer at nominally room temperature suffers from a similar or even stronger fragmentation than it shows beyond its thermal decomposition temperature over 440°C [20].

Early gas chromatographic studies on the thermal degradation of PE showed that a large number of different alkanes and alkenes are formed. Tsuchiya and Sumi collected the degradation products on a squalene column and identified aliphatic hydrocarbons from methane to hexane, both saturated and unsaturated, in the chromatograph [21]. Bockhorn et al. investigated the thermal degradation of polyethylene by mass spectrometry measurements of the degradation products in a stream of helium at reduced gas pressure [15,22]. They found *n*-alkanes and *n*-alkenes, particularly CH_x, C_2H_x, and C_3H_x. The degradation is based on random scission of the polymer chain into primary radicals, accompanied by intra- and intermolecular hydrogen transfer. Petersen et al. reported that propene and hexane are most abundant [23].

In general, it can be stated that the thermal bond scission in PE is random. In first order, all bonds are identical. When the dissociation energy is reached, C-C bonds start breaking in different places, leading to fragments of different lengths.

Under ion irradiation of the polymer at ambient temperature, the same small alkanes and alkenes are to be found, but no larger ones can be detected under the given conditions.

Nedel'ko et al. studied the thermal degradation of branched PEI of different molecular weights (3,000; 20,000; 40,000 Da) in nitrogen and vacuum [16]. By means of mass spectrometry, they found ammonia, ethylamine, pyrrole and C-substituted ethylpyrroles as main products. Their degradation mechanism starts with the fracture of the C-N bond, forming a terminal amino group and a C=C bond. Apparently, ammonia is formed by further C-N bond fracture, followed by transfer of hydrogen. Also, the formation of ethylamine and the one of pyrrole is a consequence of the fracture of 2 C-N bonds, in different distances from the N atom, with ring formation as a follow up reaction in case of pyrrole, and ethylpyrroles. In a further study, the same group investigated N-methyl-substituted PEI [17]. In analogy to ammonia as the main decomposition product of PEI, here, methylamine and methylethylamine were found.

Here, the situation is different from PE. There is a significant difference in the bond dissociation energies. While the average dissociation energy between C atoms is around 347-356 kJ/mole (corresponding to 3,6 eV), it is only 293 kJ/mole for the polarized C-N bond. The largest amount of energy is required to cut the C-H bond with 439 kJ/mole (4.5 eV). That means that upon heating PEI, first C-N bond fracture will take place [24,25].

Compared to thermal decomposition, the molecular fragments of ion beam degradation are smaller, with small primary amines and small hydrocarbons being the majority.

In case of PA6, there is a similarity to PEI's thermal degradation. The mechanism is primarily based on the fracture of the C-N bond. Bockhorn et al. showed by means of mass spectrometry that the main thermal decomposition product of PA6 is caprolactam and its fragments at m/z = 113, 85, 84, 56, 55, 43, 42, and 30. Smaller masses in the spectrum, such as m/z = 17, 18 or 44 were not considered. Herrera et al. investigated the thermal degradation of different polyamides, including PA6 in nitrogen [18]. They state that the weight loss takes place between 350°C and 475°C. Mass spectrometry showed the light volatile products of the mass-to-charge ratio m/z = 15, that is the fragment NH from NH_3, 18 from H_2O, 27 from HCN, and 44 from CO_2. When the PA6 was burned at 800°C in nitrogen and the reaction products were adsorbed and then measured via GC-MS, the main product found was caprolactam, i.e. the monomer of PA6, but also nitriles (butane, pentane, hexane) and cyclic compounds, such as cyclopentenone, were found [26].

In contrast, in ion irradiation of PA6 no caprolactame nor its larger fragments were found. Only small molecules of N- and O-containing (hydro)carbon-compounds were identified.

5. Conclusion

The degradation of the polymers is based on bond scissions that take place when sufficient energy is introduced. The bond dissociation energy can either be supplied by the energetic ions via electronic excitation, or it can classically be provided by heat leading to vibrations and eventually to dissociation. Thermal degradation in inert gas or vacuum is essentially based on the bond fracture of the weakest bond. The fracture products are the molecular fragments and reaction products thereof, mostly with hydrogen involved.

The situation with ion irradiation based degradation is quite different. First, the energies involved are far beyond thermal energies. Secondly, the damage is highly localized. Thirdly, the primary processes are very fast. When the ion passes the polymer, it transfers energy to the electronic system. Electrons easily reach energy levels that allow them to leave their atoms the first step, and transfer energy to neighbouring electrons and set them free as well in the second step. The transferred energies are in the range of several 1000 eV per nm ion track. The dissociation energies of the C-H, C-C and C-N bonds are below 5 eV. That means that in contrast to thermal degradation, all bonds can be broken. Thus these bond scissions take place in large quantities in a small volume. This is the reason why many small molecular fragments are formed, and even hydrogen is set free in large quantities. The process is a non-equilibrium process, which is limited to the first nanometers around the ion trajectory. A part of the fragments can leave the polymer by means of diffusion, a part will carry out secondary chemical reactions and will either also leave the polymer into vacuum or will stay in the solid that is at room temperature after thermalization. That means that the first part of the degradation processes is extremely hyperthermal, where the rules of organic chemistry do not apply, while the second is based on standard organochemical reactions of the formed molecular fragments that are often radicals.

In the core of the ion track, the differences in bond energies will certainly not play a role since the energy level is extremely high. In the surroundings, however, where the energy is at lower levels, the different strengths of carbon-carbon bonds and carbon-heteroatom bonds play a role and lead to the observed differences in the degradation stabilities between the investigated three aliphatic polymers.

For applications in radiation fields with highly energetic heavy particles, both in space or accelerator facilities such as FAIR, an according selection of polymer types is therefore recommended.

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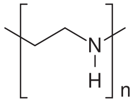
b



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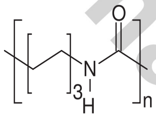

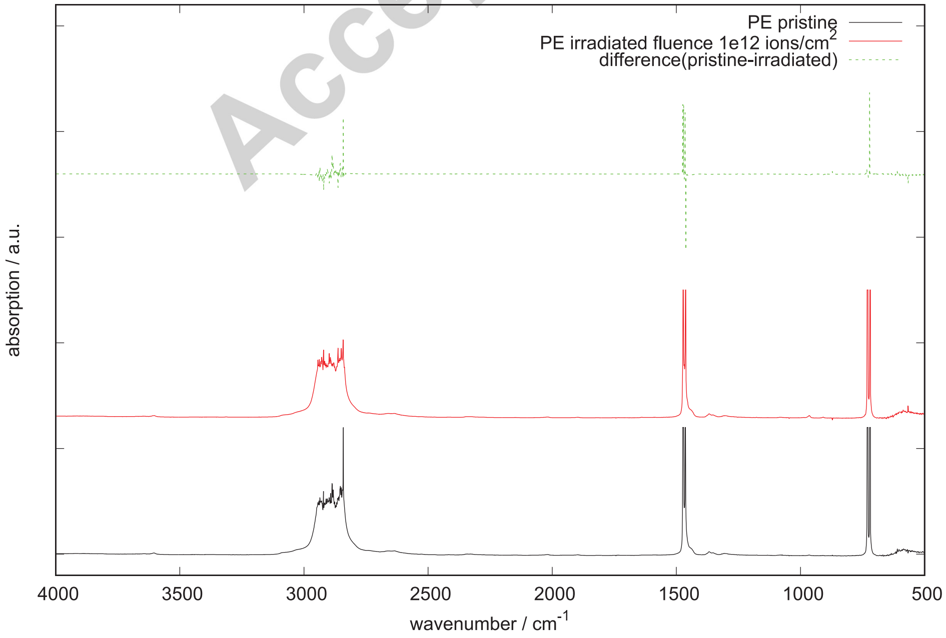
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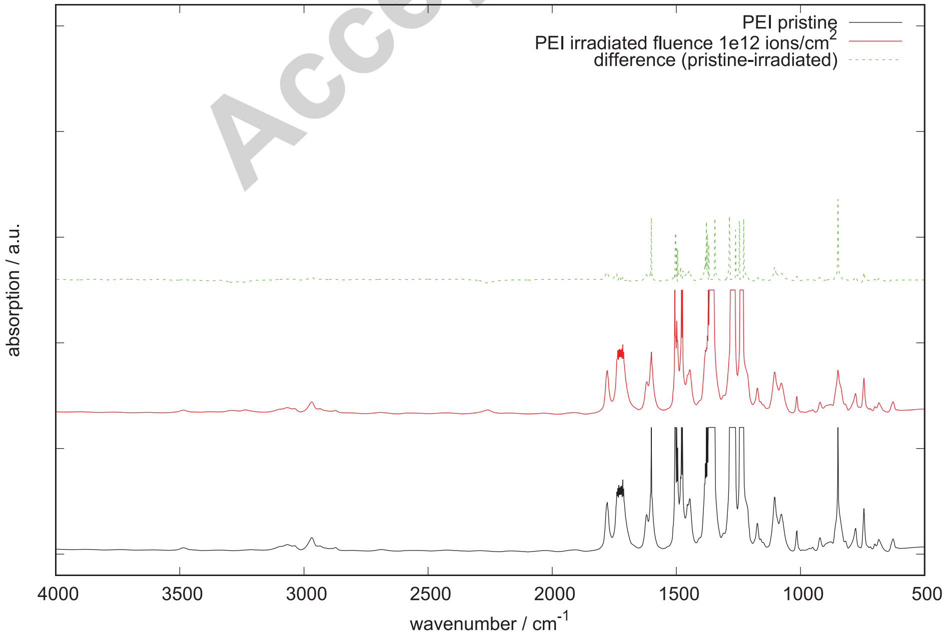
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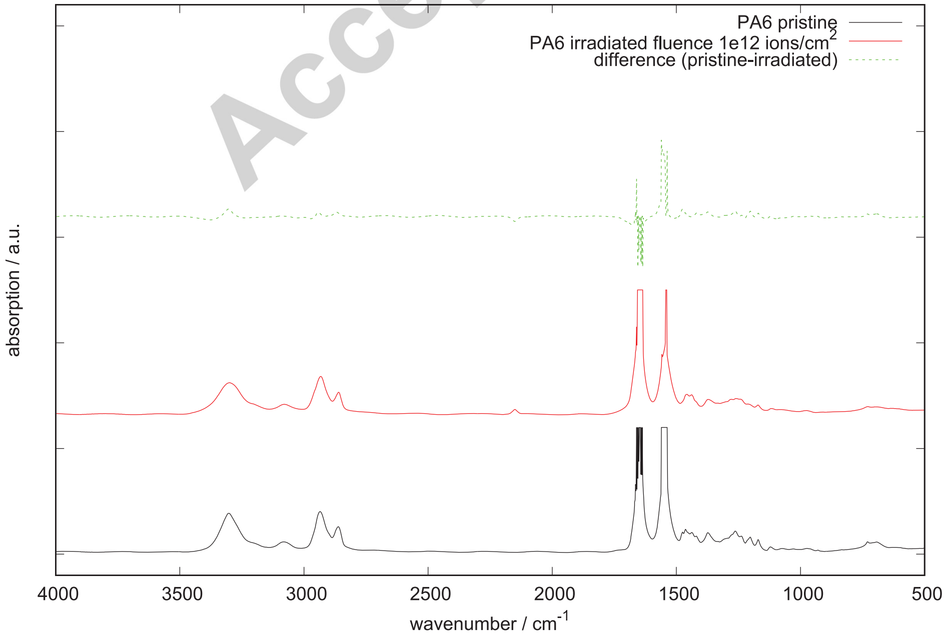
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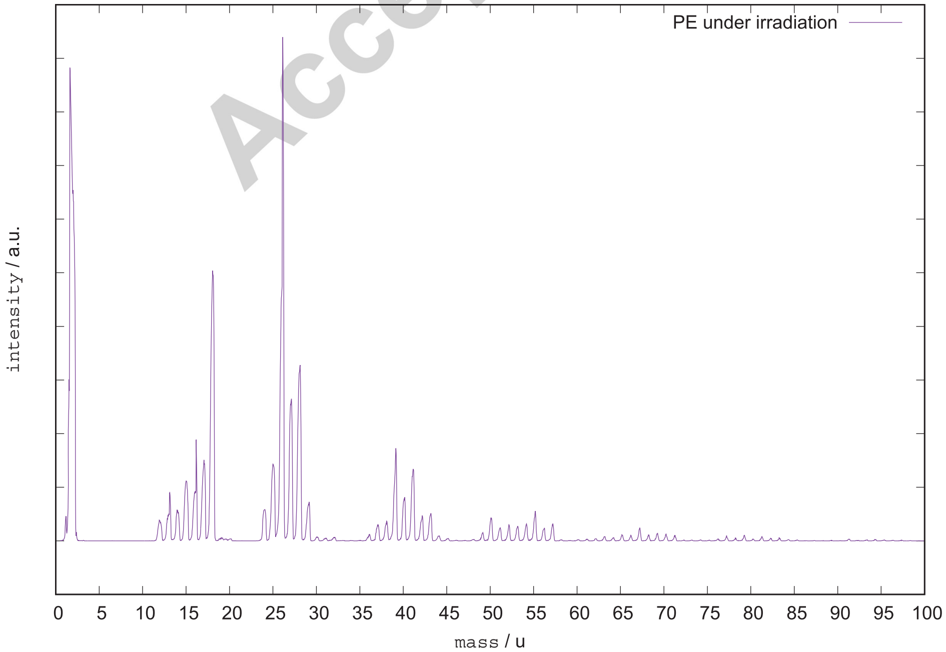
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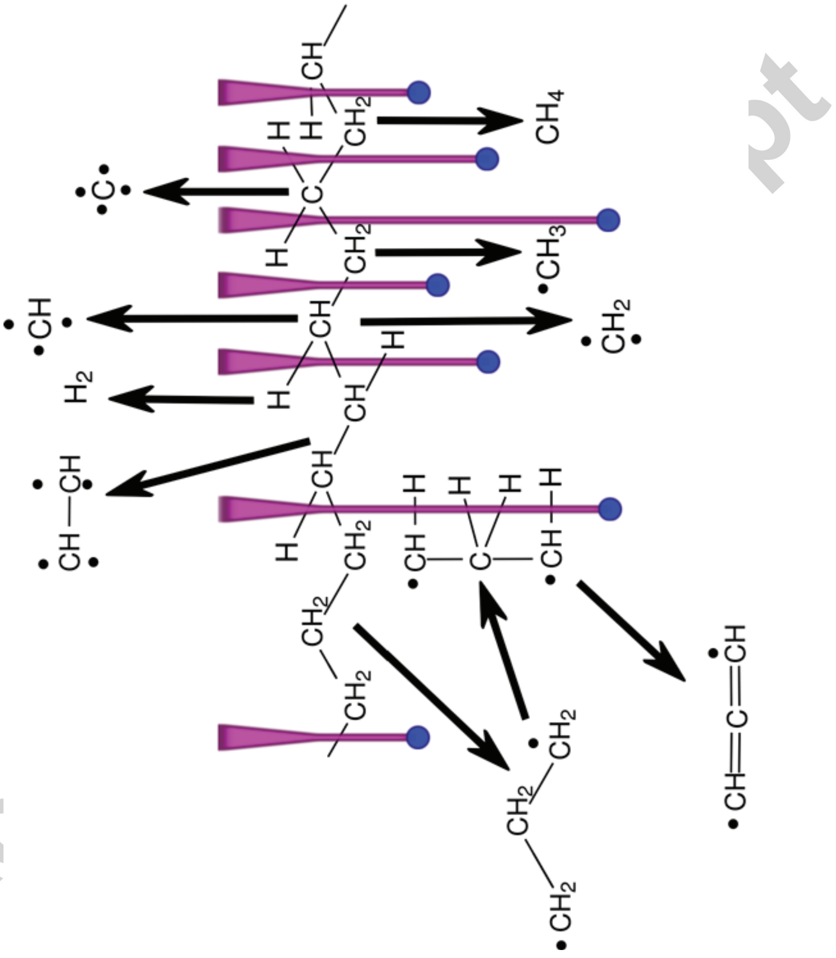
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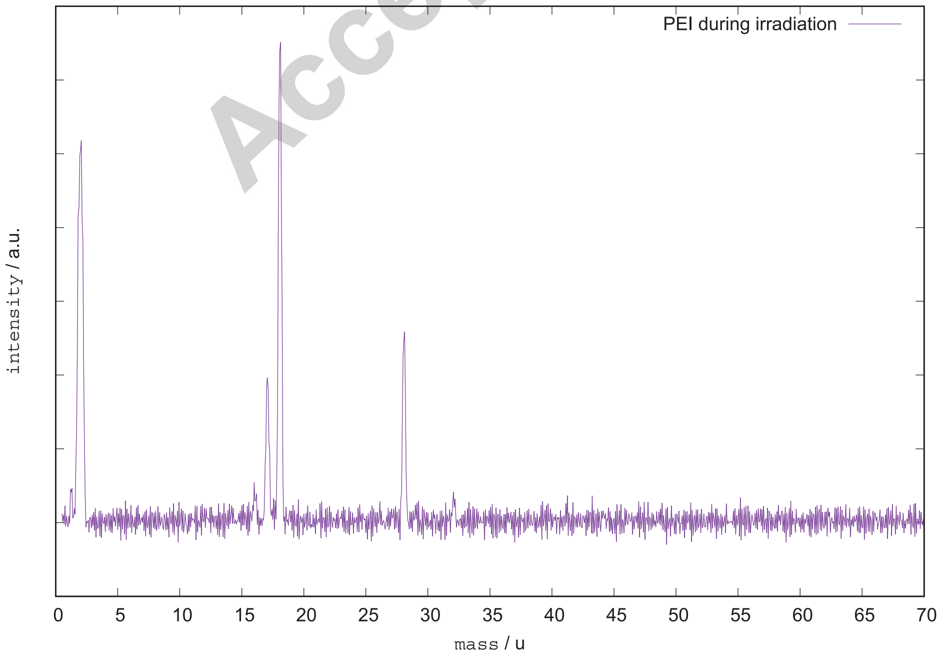
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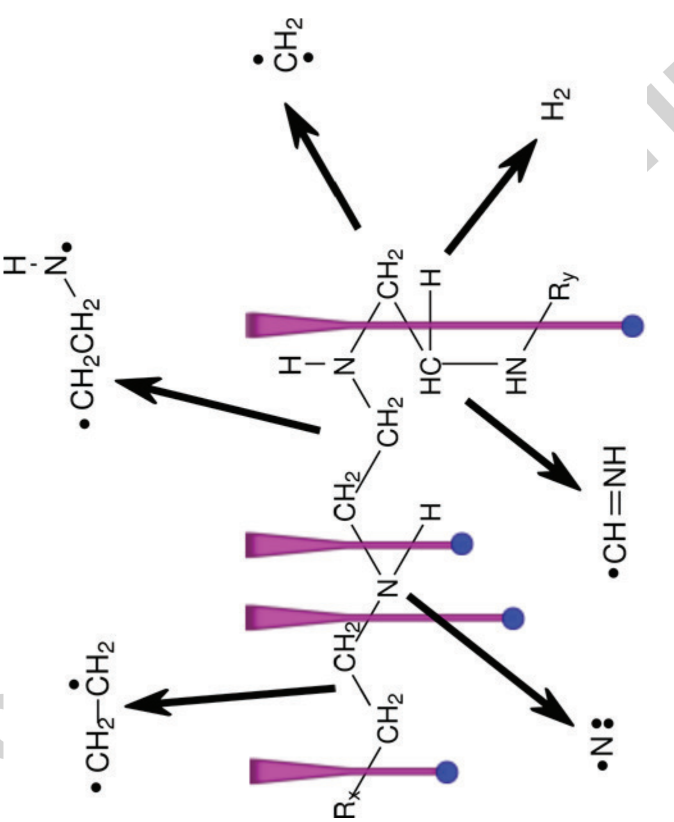
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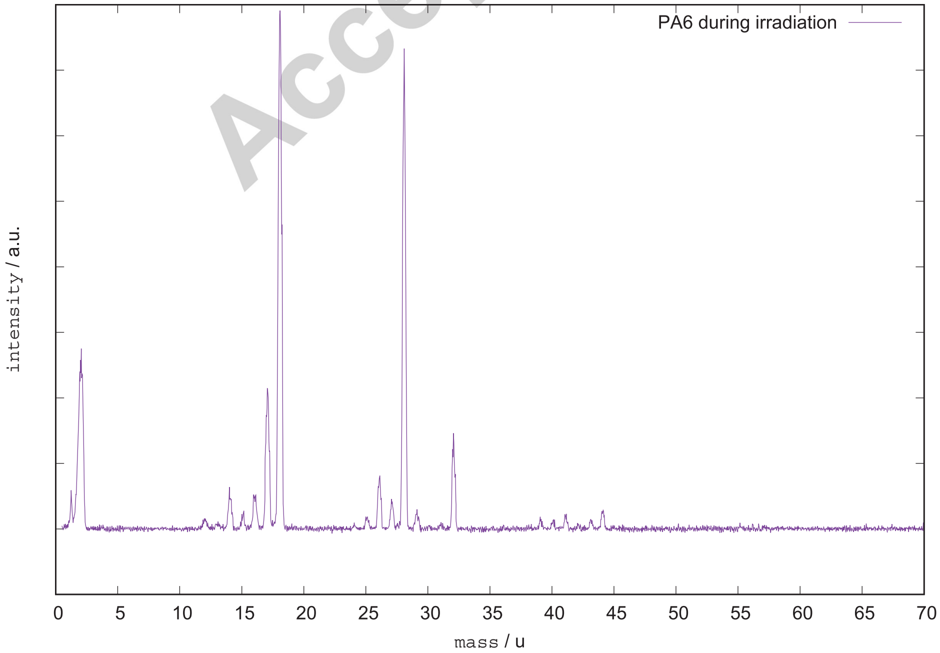
PA6 during irradiation
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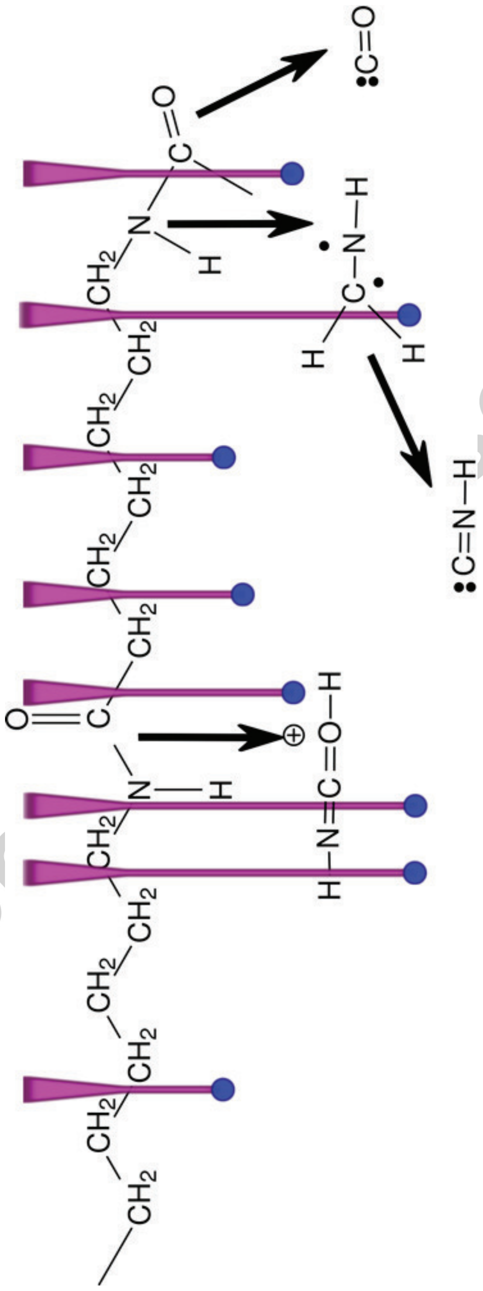
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⊕