

Analytical pyrolysis of polyethyleneimines

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Abstract

Poly(ethylene imine) is a family of polymers with a high content of amine groups employed in various applications and widely investigated as CO₂ adsorbents in carbon capture and sequestration. In this study, five branched polyethylenimines (PEIs) of different molecular weights were analysed by Py-GC-MS to gather information on the chemical structure of the principal thermal degradation products. All the PEIs produced pyrolysates with a similar chemical composition characterised by the occurrence of ethylenediamine, diethylenetriamine, piperazine, *N*-ethylaminepiperazine, pyrazine, 2-methylpyrazine, 2,3-dimethylpyrazine, 2-ethylpyrazine. Oligomeric ethylene polyamines were volatilised or evolved after chain scission of the PEI backbone. Pyrolysates also contained minor amounts of alkylated pyrroles, imidazoles, pyridines and other compounds that could not be identified. Pyrolysis products were formed at 300 °C, and their abundance increased markedly from 400 to 600 °C. Pyrolysis of PEIs at 500 °C in the presence of mesoporous silica favoured cyclisation and aromatisation, enhancing the production of alkylated pyrazines. These compounds are of potential interest in the food industry as flavour-enhancing additives.

1. Introduction

Poly(ethylene imines) are a large family of aliphatic polyamines characterised virtually by the $-\text{CH}_2\text{CH}_2\text{NH}-$ structural unit. They are also named as polyaziridines being synthesised from the aziridine monomer by cationic ring-opening polymerisation. This synthetic route does not produce the linear polyethyleneimines, but instead leads to the formation of branched polymers. Branched polyethyleneimines (herewith abbreviated as PEIs) present in their structure tertiary amine groups in addition to primary and secondary ones [1,2].

Despite the challenges in controlling the polymerisation reaction to produce PEIs with definite molecular weight (MW) and dispersity, these polymers have found applications in many fields where properties associated to a high number of nitrogen atoms in the macromolecule are required, such as flocculant (clarification agents) in paper-making industries and metal chelator in water purification, ingredients in household products and cosmetic manufacturing [1]. PEIs are attracting growing interest, especially in biomedicine and biotechnology as drug delivery and gene carrier systems [3].

PEIs have been investigated intensively as high MW amines capable to react reversibly with CO_2 in CCS (carbon capture and sequestration) processes. Attention has been focused on adsorbents that combine PEI with porous siliceous materials to the end of developing CCS processes with improved performance over those traditional, based on low MW amine-aqueous solution systems employed in hard for abate industrial emissions [4,5]. Silica-PEI systems have also been studied to directly capture CO_2 from the atmosphere since 2011 [6].

Although PEIs constitute an important class of polymers, their thermal behaviour at the molecular level has not been investigated in depth, and only a few studies have been published. The thermal degradation of PEI under nitrogen at temperatures from 230 to 321 °C was reported by Nedel'ko *et al.* [7]. The authors have found that the activation parameters were not dependent on the molecular weight of PEI (MW = 3 000, 20 000 and 40 000 Da) and activation energy was around 32 kcal mol⁻¹. The principal mechanism of degradation proposed by the authors involved the cleavage of the C-

N bond followed by migration of the methylene hydrogen. Ethylamine, pyridine and pyrrole were the pyrolysis products identified by GC analysis, while alkylated pyrroles were proposed from MS analysis based on the series of ions at m/z 80, 94, 108, 122 at 200 °C [7]. However, the experimental details were scant, and the above reported ion series would also be in accordance with pyrazines. A similar study published by the same research group on linear *N*-methyl and *N*-benzoyl PEI highlighted the importance of heat stability upon substitution of the nitrogen atom, lower for *N*-methyl and higher for *N*-benzoyl groups [8]. Here, *N*-methyl and *N*-dimethyl piperazines were identified thermal degradation products of *N*-methyl PEI, while piperazines were not reported for branched PEIs [8]. Instead, piperazine derivatives were identified in the pyrolysates of PEI with a *tert*-butyl group on nitrogen after cleavages of the C-N bonds followed by rearrangement [9]. The importance of *N,N*-substituted piperazines as thermal degradation products of variously *N*-substituted PEI was highlighted by Barb [10].

The interest in the heat stability of PEI has increased in recent years due to their use in the sorption and release of CO₂ in CCS process. However, most studies were conducted at sub-pyrolysis temperatures and were not informative at molecular levels. The pyrolytic behaviour of PEI-C60 was investigated by X-ray photoelectron spectroscopy (XPS), Fourier transfer infrared (FTIR) and Raman revealing a conversion towards disordered graphitic carbon including pyrrole and pyridine-like structures [11]. The chemical nature of the evolved thermal degradation products remains elusive, and a better understanding of this aspect is the main objective of this study.

Analytical pyrolysis combined with gas chromatography-mass spectrometry (Py-GC-MS) is notoriously a powerful technique for the analysis at a molecular level of the chemical composition of pyrolysates. Here, we show for the first time the results arising from the application of Py-GC-MS to understand the nature of the products evolved from the thermal decomposition of PEI. The effect of active silica was also investigated, given the increasing attention on silica-PEI systems for implementing CCS and the need for information about their thermal behaviour.

2. Materials and methods

2.1 Materials

Polyethyleneimines PEI 800 (Mw = 800 Da, 98 % w/w), PEI 1300 (Mw = 1300 Da, 50 % w/w), PEI 750000 (Mw = 750000 Da, 50 % w/w) were purchased from Sigma-Aldrich; PEI 2000 (Mw = 2000 Da, 50 % w/w) and PEI 25000 (Mw = 25000 Da, 48-56 % w/w), ; from BASF.

Solutions were prepared by dissolving PEI solutions (exactly weighted) in methanol to obtain PEI concentrations of 50 mg mL⁻¹ for PEI 800 and 25 mg mL⁻¹ for PEI 1300, 2000, 750000 and 25000 (assuming 50 % w/w PEI concentration). A volume of 5 µL of each solution was analysed by Py-GC-MS.

Pyrazine, 2-methylpyrazine, 2,3-dimethylpyrazine, 2,5-dimethylpyrazine, 2-ethylpyrazine, 2-propylpyrazine, 2-ethyl-3-methylpyrazine, piperazine, ethylenediamine, diethylenetriamine (*N*-(2-aminoethyl)ethane-1,2-diamine), *N*-aminoethylpiperazine (1-piperazine ethanamine or *N,N*-dimethyl-2-piperazin-1-ylethanamine), triethylenediamine (or 1,4-diazabicyclo[2.2.2]octane, also known as DABCO) and triethylamine were purchased from Sigma-Aldrich. Methyl palmitate from Sigma-Aldrich was used as the internal standard (125 µg mL⁻¹ in methanol).

A commercial mesoporous silica (specific surface area 305 m² g⁻¹ (BET), pore total volume 1.75 cm³ g⁻¹, 91 % mesopores) was used to study the effect of active solids on the pyrolytic behaviour of PEIs.

2.2 Py-GC-MS

Py-GC-MS experiments were performed using a multi-shot pyrolizer (EGA/PY-3030D Frontier Lab) connected to a gas chromatograph (7890B Agilent Technologies) interfaced to a quadrupole mass spectrometer (5977B Agilent Technologies). For each experiment, 5 µL of the PEI methanolic solution and 2.5 µL of the internal standard solution were introduced inside a cup containing quartz wool or 5 mg of mesoporous silica. [Pyrolyses were also performed with \(5 mg\) and without silica on the model compounds diethylenetriamine and 1-piperazine ethanamine \(5 µL of methanolic](#)

solution containing 50 μg of amine). Samples were left at room temperature for some minutes to favour methanol evaporation. Pyrolysis were conducted at 500 $^{\circ}\text{C}$ unless otherwise specified. The pyrolysate was introduced (Py-GC interface 300 $^{\circ}\text{C}$, 1:50 split conditions) into the GC column fused silica capillary column (HP-5MS, stationary phase 5%-diphenyl, 95 %-dimethylpolysiloxane 30 m \times 0.25 mm i.d. \times 0.25 μm film thickness). The gas chromatograph was operated in a constant helium flow 1.0 mL min^{-1} . The oven programmed temperature started at 40 $^{\circ}\text{C}$, held for 5 min, and then it was ramped at 5 $^{\circ}\text{C min}^{-1}$ to 250 $^{\circ}\text{C}$, where it was held for 3 min. Mass spectra were recorded under 70 eV electron ionisation in the m/z 30–600 interval at 2.6 scan sec^{-1} . The temperature of the ion source and the quadrupole were 230 $^{\circ}\text{C}$ and 150 $^{\circ}\text{C}$, respectively. Py-GC-MS analyses were run in duplicate or triplicate. Compound identification was based on injection of pure compounds, Kovats' retention indices when available, NIST 14 library match and comparison with literature.

2.3 TGA

The effect of silica was further investigated by TGA on a selected PEI. Samples of raw PEI 2000 and silica impregnated with PEI 2000 (50% wt. % on a dry basis) were analysed using a TA Instruments Thermogravimetric Analyser Q500 (TGA Q500) under 100% nitrogen (100 ml/min, 1 bar). Samples were heated from ambient to 110 $^{\circ}\text{C}$ at a ramp rate of 30 $^{\circ}\text{C min}^{-1}$, and held isothermally for 15 minutes to remove moisture. The raw PEI sample was held isothermally for 30 minutes to remove all bound water within the amine layers. Next, the samples were cooled to approximately 90 $^{\circ}\text{C}$, the second heating phase was started to increase the temperature to 800 $^{\circ}\text{C}$ at 30 $^{\circ}\text{C}/\text{min}$. At 800 $^{\circ}\text{C}$, the samples were held isothermally for 15 minutes to determine ash in raw PEI, and remaining silica in the Si-PEI impregnated samples. Weight loss between 200-700 $^{\circ}\text{C}$ was used to determine the onset of PEI volatilisation, and the loading of the Si-PEI sample.

3. Results

3.1 Py-GC-MS of PEI 800. Identification of evolved products

Figure 1 shows exemplar pyrograms obtained from PEI 800 pyrolysed at different temperatures. At 300 °C the pyrogram was characterised by a suite of products at relatively high retention times whose intensity decreased with increasing pyrolysis temperature. They were tentatively attributed to oligomers of linear and branched ethylene polyamines volatilised or formed upon pyrolysis by chain scission. Partial volatilisation of PEI at sub-pyrolysis temperatures has been reported [12]. Oligomers were fragmented at high pyrolysis temperatures in favour of short chain fragments, like ethylenediamine ($\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$). The attribution of these compounds was supported by the presence in the mass spectra of peak ions differing by 43 u (corresponding to the mass of the ethyleneamine fragment $\text{-NH-CH}_2\text{-CH}_2\text{-}$) at m/z 30 (assigned to $\text{NH}_2=\text{CH}_2^+$), m/z 73 ($\text{H-[NH-CH}_2\text{-CH}_2\text{-]}_1\text{-NH}=\text{CH}_2^+$), m/z 116 ($\text{H-[NH-CH}_2\text{-CH}_2\text{-]}_2\text{-NH}=\text{CH}_2^+$) and m/z 159 ($\text{H-[NH-CH}_2\text{-CH}_2\text{-]}_3\text{-NH}=\text{CH}_2^+$). In line with our observation, a series of ions separated by 43 u was observed in the ESI-MS of low MW PEIs consistent with the NH_2 terminated oligomers distinctive of the polymer composition [13]. The m/z 44 peak was assigned to $\text{CH}_3\text{-NH}=\text{CH}_2^+$. Ethylenediamine (the linear oligomer with 2 N atoms) and diethylenetriamine (the linear oligomer with 3 N atoms, see Figure 2) were confirmed by the analysis of the pure compounds (Table 1). Triethylenetetramine (4 N atoms), tetraethylenepentamine (5 N atoms) tentatively identified by similarity with library mass spectra (70-80 % match ranked # 1 in the list without background correction). The m/z 99 ion was also a ubiquitous ion that was assigned to $\text{CH}_3\text{-CH}_2\text{-NH-CH}=\text{CH-NH}=\text{CH}_2^+$, but it could be assigned to the *N*-methylenepiperazinium cation as well. The presence of oligomers containing the piperazine ring has been reported in the literature by means of GC-MS with chemical ionisation [14]. Interestingly, the authors used the same GC non-polar stationary phase in our study to separate polyethylenimines linear, branched, cyclic and acyclic homologs with up to 10 nitrogen atoms.

The production of pyrazines was negligible at 300 °C, became evident at 400 °C, and their relative intensity increased with increasing pyrolysis temperature (Figure 1). Pyrazines were present in a

variety of alkylated forms dominated by 2-methylpyrazine, 2,3-dimethylpyrazine and 2-ethylpyrazine. Interestingly, pyrazines were observed as degradation products of ethanolamine under process conditions of post-combustion CO₂ capture and the most abundant were pyrazine > 2-methylpyrazine > 2,3-dimethylpyrazine/2-ethylpyrazine similarly to our study [15]. The proposed mechanism of formation involved oxidation and reactions with aldehydes which of course could not be applied to our pyrolysis conditions.

Besides pyrazines, other aromatic amines were tentatively identified at lower proportions, such as pyrroles, pyridines, imidazoles variously alkylated (Table 1).

A simplified mechanism of formation of the main pyrolysis products so far discussed is depicted in Figure 2. Emphasis was given to the cleavage of C-N bonds, which have slightly lower bond dissociation energy than C-C bonds; even though less favoured, the dissociation of C-C bonds can also occur [16]. Cleavage of C-N bonds was observed in collisional fragmentation of quasi molecular ions of PEI oligomers upon soft ionisation [13]. Thus, chain scission at the C-N bonds is thought to be responsible for the formation of linear aliphatic polyamines, in Figure 2, exemplified by ethylenediamine and diethylenetriamine.

The formation of piperazines from a radical mechanism was proposed by Lepaumier *et al.* [2010] [17] under oxidative conditions; the intermediate is a quaternary ammonium ion that is prone to elimination following the nucleophilic attack of the nitrogen atom on the alpha carbon adjacent to the charged nitrogen. The presence of ionised nitrogen atoms could favour the formation of piperazines from intermolecular reactions of linear amines, as for instance coupling of two ethylenediamines. In the example of Figure 2, the intermolecular formation of the piperazine ring would be favoured by a proper conformation of the polymer chain.

3.2 Py-GC-MS of PEI 800. Effect of silica

Mesoporous silica also had a remarkable effect on the abundance and distribution of the pyrolysis products, as one can see by comparing the intensity of peaks in the pyrograms shown in Figure 1 (at 500 °C) without silica and Figure 3 with silica. In comparison to the internal standard, it is evident the increased formation of piperazines and pyrazines in the presence of silica. This finding indicates that silica promoted cyclization reactions of linear oligomers or PEI backbone. The propensity to cyclization is highlighted by the presence of a tricyclic diamine, triethylenediamine (DABCO) (Table 1). As a result, the linear diethylenetriamine was not detected.

The presence of SiO₂ caused a remarkable increase of alkylated pyrazines, principally 2-methyl, 2,3-dimethyl and 2-ethylpyrazine. Similar behaviour was observed for piperazines for which different methylated species were tentatively identified (e.g. 1-methyl and 1,4-dimethyl, Table 1). Several GC peaks exhibited mass spectra with an intense ion at m/z 99 assigned to *N*-methylenepiperazinium ion (section 3.1).

The propensity of silica to promote cyclisation, aromatisation and alkylation was supported by the pyrolysis of diethylenetriamine and 1-piperazine ethanamine (Figure 4). Py-GC-MS of 1-piperazine ethanamine produced triethylenediamine (DABCO), pyrazine, 2-methylpyrazine, 2,3-dimethylpyrazine, 2-ethylpyrazine (Figure 4). Piperazine and *N*-methylpiperazine were also formed suggesting that 1-piperazine ethanamine is an appropriate model compound for studying the pyrolytic behaviour of PEI. Instead, diethylenetriamine produced essentially pyrazines when pyrolyzed in the presence of silica, while piperazines and the original substrate were not observed suggesting that thermal degradation was more severe for acyclic than cyclic oligomers. Alkylated pyrazines were not detected as impurities by direct GC-MS analysis of the model compounds, while pyrazine was barely detected. This finding confirmed that pyrazines were formed upon pyrolysis and not by volatilisation of pyrazines originally present in the standard substances.

Surprisingly, pyrazines with a high degree of alkylation (C3-pyrazines) were also observed at significant levels, in particular propylpyrazine and 2-ethyl-3-methylpyrazine. The formation of C3-pyrazines is difficult to rationalise through intramolecular reactions of the PEI backbone that

contains C2-N units. It could be explained by reactions of coupling of alkyl radicals and the formation of intermediates such as ethylene or propylene followed by alkylation of pyrazines. The formation of higher molecular weight hydrocarbons from the pyrolysis of aliphatic amines has been reported and explained as the result of termination reactions between the alkyl radicals formed during pyrolysis [16]. A similar mechanism was proposed to describe the formation of alkylamines and hydrocarbons produced by the pyrolysis of simple amines in the presence of TiO₂ [18].

3.3 Py-GC-MS of PEI with different molecular weight.

Pyrograms of the different PEI, conducted at 500 °C, appeared rather similar and did not display any obvious trend with increasing MW (Figure 5). The most relevant pyrolysis products that could be reliably identified were low MW linear polyamines, piperazines and pyrazines without evident differences in their distribution. This finding would indicate that under the experimental conditions of this study, Py-GC-MS was unable to highlight possible differences in the degree of branching. The degree of branching can be associated to the relative ratios of primary/secondary/tertiary amine groups which was not measured here. Presuming that these ratios are those reported by a manufacturer of PEIs in a technical report (“Lupasol® types” 08_0806130e-02, 2010, BASF) the values would be 1/0.9/0.5, 1/0.9/0.6, 1/0.9/0.6, 1/1.1/0.7, 1/1/0.7 for 800, 1300, 2000, 25000, 750000, respectively. These ratios were rather similar regardless the MW, as evidenced in the literature [19]. Although the theoretical ratio of primary/secondary/tertiary amines was calculated to be 1/2/1, the ratio in commercially available products is closer to 1/1/1, indicative of higher branching [2]. Even though the relative proportion of tertiary amines appeared to slightly increase with increasing MW, the change was probably insufficient to be captured by Py-GC-MS. Most of the pyrolysis products formed broad peaks with overlapping mass spectra and could not be identified, even though the common presence of ions at m/z 44, 99, and 116 suggested the presence of aliphatic polyamines (see section 3.1). Although not identified by analysis of pure analytes, these

oligomers appeared to be released at higher relative intensity from low MW PEIs.

Thermogravimetric analysis (TGA) up to 700 °C in the presence of oxygen showed a similar behaviour of PEIs with different MW; only a slightly higher thermal stability was observed for the polymers with higher MW (10000 and 60000) that remained almost intact until above 300 °C [19]. The presence of silica influenced differently the decomposition of PEIs with different MW (Figure 6). The most noticeable effect was the decrease of the peak intensity of aliphatic amines, particularly piperazines (piperazine, methyl piperazine and *N*-aminoethylpiperazine) and ethylenediamine with increasing MW. These pyrolysis products produced intense peaks in the pyrograms of PEI 800, and weak peaks in the pyrograms of PEI 25000 and PEI 750000. Instead, these latter PEIs with high MW exhibited a higher relative intensity of a group of pyrolysis products tentatively identified as alkylated 1*H*-imidazoles. We were unable to identify the possible reason of the decreasing amount of aliphatic amines and increasing amount of alkylated imidazoles with increasing MW. As seen above, PEIs with higher MW could have a higher degree of branching that favoured the formation of aromatics, including imidazoles. Other factors to be investigated could be the different chain end concentration and viscosity of the various PEIs.

Pyrazine, 2-methylpyrazine, 2,3-dimethyl and 2-ethylpyrazines remained the dominant pyrolysis products of all the PEIs.

The influence of silica on the pyrolytic behaviour of the polyamines was confirmed by TGA of PEI 2000. The onset of volatilisation started at 270-280 °C for raw PEI and at lower temperature, around 200 °C, for PEI loaded on silica.

TGA under N₂ of different silica-PEI systems indicated a rapid weight loss in the 200-500 °C temperature range that was the highest in the 200-300 °C interval for the PEI with the lowest MW (800 Da) [20]. This last finding was attributed to the volatilisation of low MW components that should be in higher proportions in PEI 800. Accordingly, our Py-GC-MS data revealed the release of oligomers from PEI 800 at a higher intensity compared to PEI with higher MW at 500 °C (Figure

5). Silica appeared to reduce the evolution of oligomers (Figure 6), even though Li *et al.* reported a weight loss between 130 and 160 °C of PEI-nano silica adsorbents that was explained by the loss of PEI molecules, while adsorbed water would be eliminated below 130 °C [20].

The production of alkyl pyrazines as a characteristic compound family from the pyrolysis of PEI is of interest due to their importance in various applications. Pyrazines are widely distributed in nature where they act as parasite repellents and in food products for their olfactory properties [21]. Among the principal pyrazines found in PEI pyrolysates, 2,3-dimethylpyrazine and 2-ethylpyrazines are used as flavouring additives in human food and animal feed.

4. Conclusions

This is the first detailed study on the thermal behaviour of branched polyethyleneimines at the molecular level performed by Py-GC-MS. Pyrolysis of these polymers with different molecular weights produced three main classes of compounds: linear aliphatic acyclic polyamines, cyclic aliphatic amines, principally piperazines, and aromatic amines dominated by pyrazines. High temperatures and the presence of silica favoured the formation of pyrazines. Besides pyrazines, other aromatic amines were formed, among them alkylated pyrroles and imidazoles. Aliphatic acyclic oligomers and piperazines featured the pyrolysates of low molecular weight polymers, while aromatic amines were the dominant products for high molecular weight polymers in the presence of silica.

The knowledge of the thermal degradation products of PEIs, pure and in the presence of porous silica, is essential in the field of carbon capture, where these materials can be prone to severe oxidation, and pyrolysis offers a means to generate potentially valuable chemicals from spent PEI. The presence of relatively high levels of pyrazines in the PEI pyrolysates could have interesting implications as pyrazines are an important class of chemicals with notable applications in food industry due to their flavouring properties.

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Table 1. GC-MS data and structural attribution of the pyrolysis products from the PEIs. RT: retention time (minutes); *m/z*: mass to charge ratio of relevant ions, base peaks are in bold, molecular ions in italics. Compound with names in bold were identified by injection of the pure compound.

Compound	RT	<i>m/z</i>
trimethylamine	1.54	42, 58 , 59
ethylamine	1.60	30 , 44, 45
ethanamine, <i>N</i> -methyl-	1.75	30, 44 , 59
ethylenediamine	2.72	30 , 43, 60
pyrazine	3.87	52, 53, 80
pyrrole	4.60	39, 41, 67
2-methylpyridine	6.39	66, 78, 93
1-ethylpyrrole	6.41	67, 80, 95
2-methylpyrazine	6.75	53, 67, 94
2 or 3-methylpyrrole	7.51	53, 80 , 81
2 or 3-methylpyrrole	7.86	53, 80 , 81
1,4-dimethyl piperazine	7.98	43 , 71, 114
1-methyl piperazine	8.03	42, 58 , 100
piperazine	8.14	44 , 56, 85, 86
dimethylpiperazine	9.37	30, 58, 99 , 113
2,5 (or 2,3) dimethylpiperazine	9.61	58 , 99, 114
2,5-dimethylpyrazine	10.0	42 , 81, 108
2-ethylpyrazine	10.1	80, 107 , 108
2,3-dimethylpyrazine	10.3	40, 67, 108
1-methyl imidazole	10.9	42, 54, 82
1,2,4-trimethylpiperazine	11.1	42, 57, 128
dimethylpyrrole	11.2	80, 94 , 95
2-propanone-1-(<i>N</i> -cyanomethylimino)	11.2	42 , 69, 110
unknown (aliphatic polyamine?)	11.3	72 , 99, 114
2-methyl, 2-imidazoline	12.4	42, 55, 84
2-ethyl-5 or 6-methylpyrazine	13.1	39, 121, 122
1 <i>H</i> -pyrazole, 3-ethyl-4,5-dihydro-1,4-dimethyl-	13.2	83, 111, 126
trimethylpyrazine	13.3	42 , 81, 122
2-ethyl-3-methylpyrazine	13.4	67, 121, 122
2-propylpyrazine	13.5	94 , 107, 122
2-ethyl-4-methylpyrrole	13.6	67, 94 , 109
Triethylenediamine	13.8	42, 55, 112
1 <i>H</i> -imidazole, 1,2-dimethyl-	13.9	54, 95, 96
2-methyl-1-vinylimidazole	14.2	41, 54, 108
diethylenetriamine	14.5	30, 44 , 73
<i>N</i> -(2-aminoethyl)- <i>N</i> -methylenediamine	14.7	44 , 58, 87
2-methyl-3-propylpyrazine	15.2	108 , 121, 136
1 <i>H</i> -imidazole, 1-ethyl-2-methyl	15.9	81, 95, 110
1-piperazine ethanamine	18.6	56, 70, 99 , 129
unknown	21.1	55 , 136, 137
triethylenetetramine	24.8	44 , 73, 99
unknown	27.2	97, 98 , 142
tetraethylenepentamine	31.8	44 , 99, 116

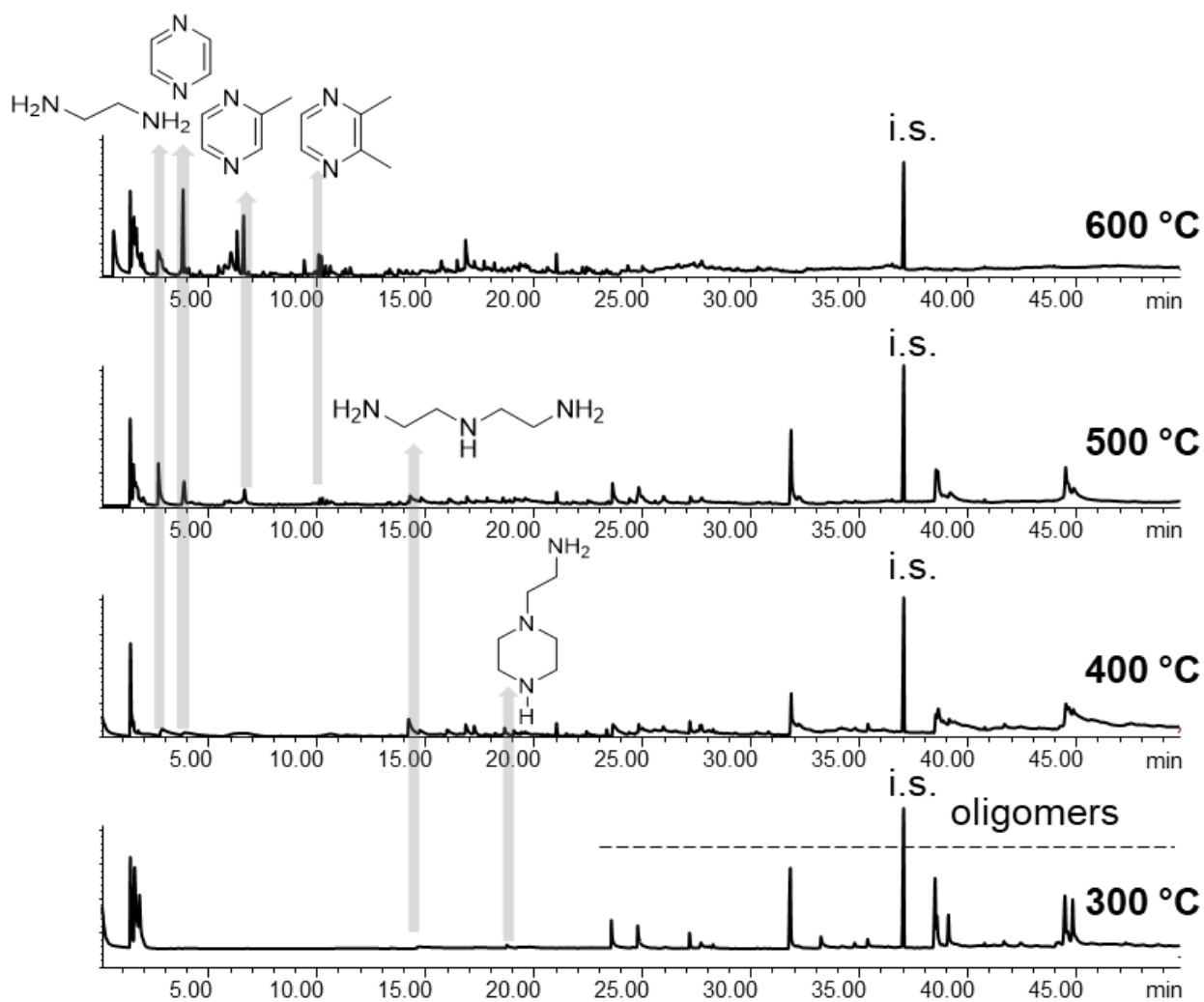


Figure 1. MS-pyrograms of PEI 800 (250 μg) at different pyrolysis temperatures. The molecular structure is presented for some compounds identified by comparison with pure standards. In the increasing elution order: ethylenediamine, pyrazine, 2-methylpyrazine, 2,3-dimethylpyrazine, diethylenetriamine (1,4-diazabicyclo[2.2.2]octane), 1-piperazine ethanamine (*N*-ethylamine piperazine).

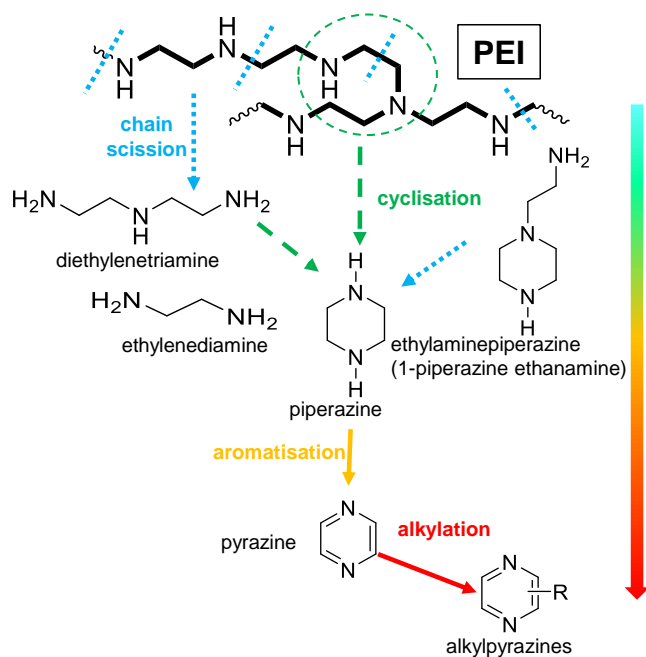


Figure 2. Simplified mechanism of the formation of pyrolysis products from branched PEI. The formation of products from the top to the bottom are favoured by increasing pyrolysis temperature and the presence of silica.

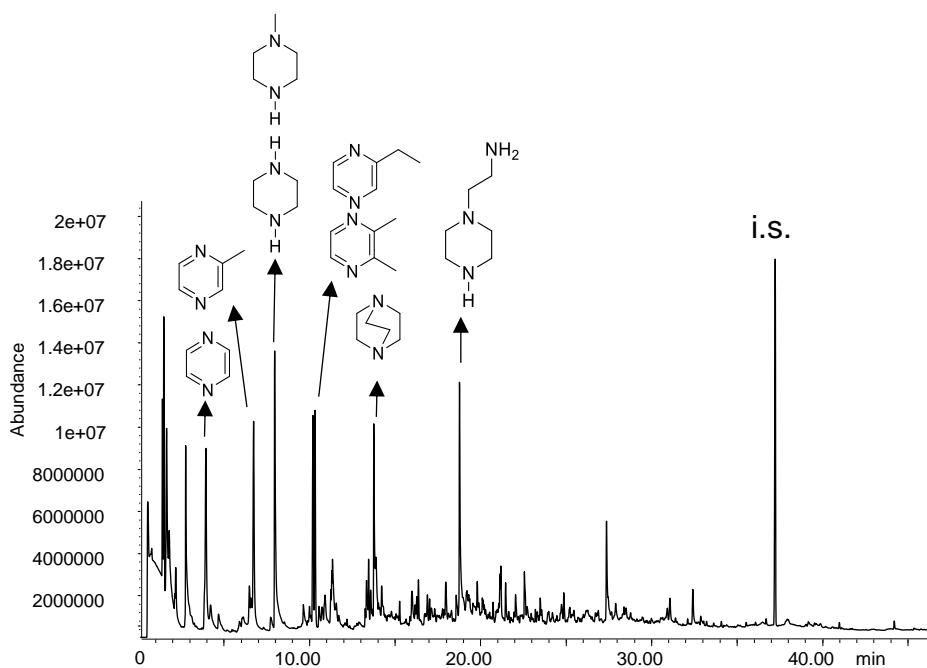


Figure 3. Pyrogram at 500 °C of PEI 800 (250 µg) in the presence of silica.

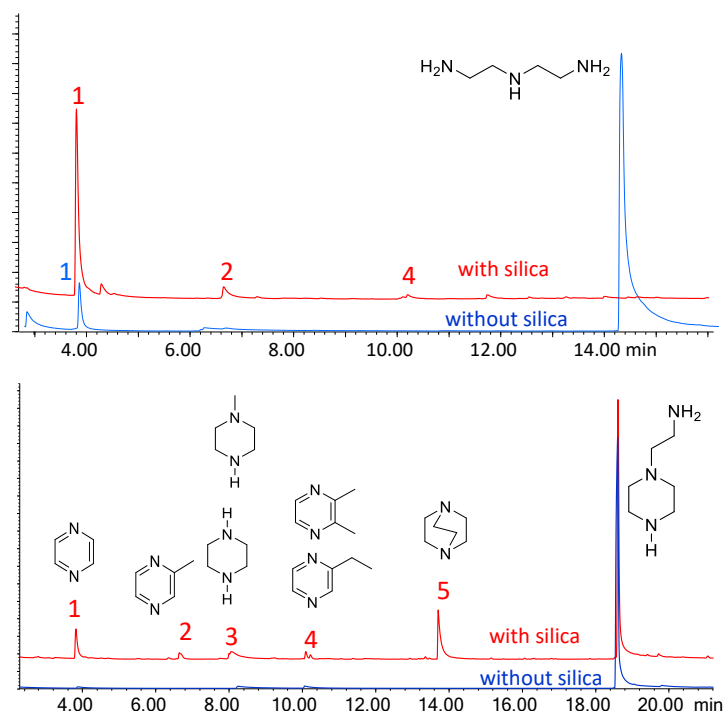


Figure 4. TIC chromatograms from Py-GC-MS at 500 °C with and without silica of diethylenetriamine (top) and 1-piperazine ethanamine (bottom). 1: pyrazine, 2: 2-methylpyrazine, 3: piperazine, methylpiperazines, 4:C2-pyrazines, 5: triethylenediamine.

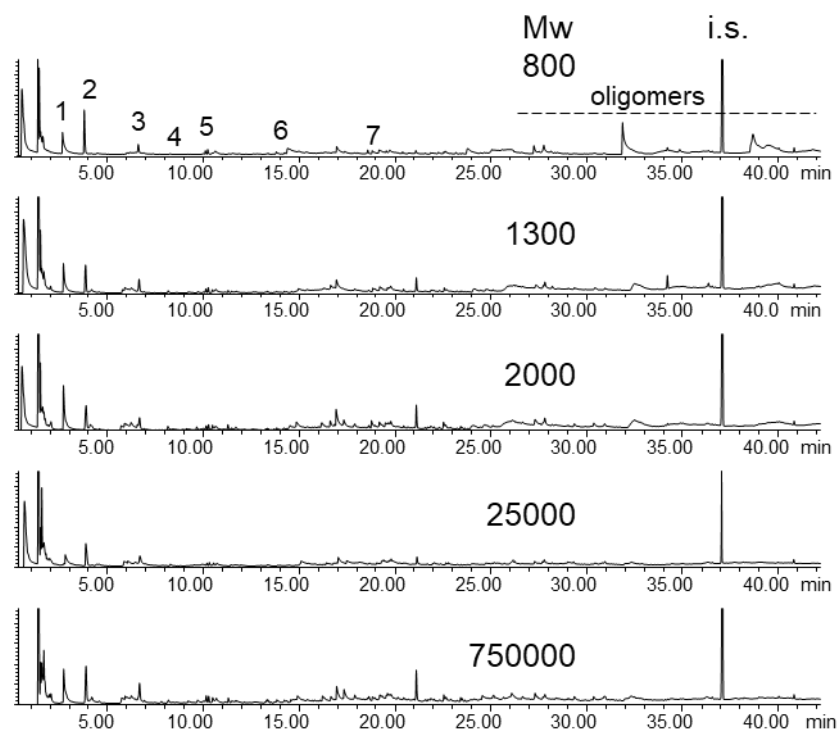


Figure 5. MS-pyrograms of PEI of different molecular weight pyrolyzed at 500 °C (all normalised at the same Y value of 8×10^6 counts; 125 μg all but PEI 800 250 μg). Product identification based on the analysis of pure compounds (the same in all the pyrograms): 1: ethylenediamine; 2: pyrazine; 3: 2-methylpyrazine; 4: piperazine; 5: 2,3-dimethylpyrazine; 6: diethylenetriamine; 7: 1-piperazine ethanamine. Internal standard: i.s.

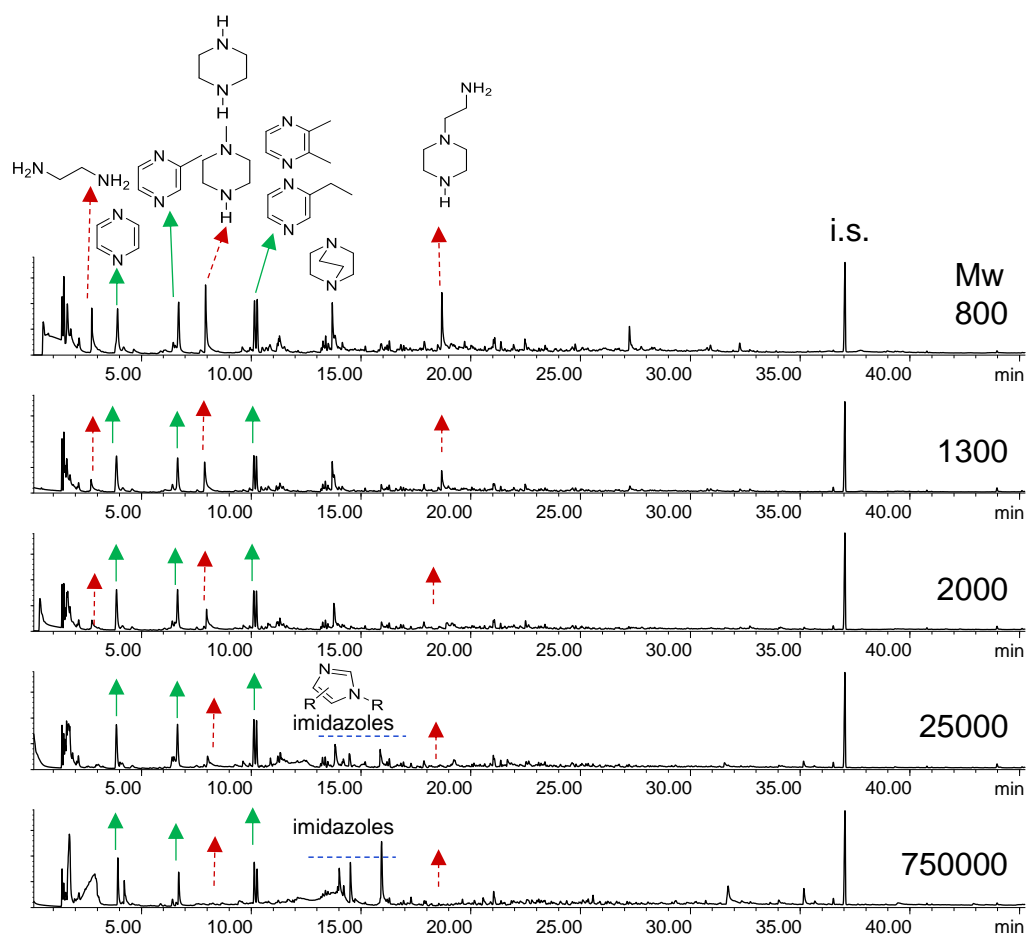


Figure 6. MS-pyrograms of PEI at different molecular weight pyrolyzed at 500 °C in the presence of SiO₂. Arrows: dashed aliphatic amines, full pyrazines. The molecular structures of compounds with similar retention times are placed vertically over