



Research article

Simultaneous thermal analysis of cationic, nonionic and anionic polyacrylamide

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ABSTRACT

Polyacrylamide (PAM) and its derivatives are the most commercially available water-soluble polymers and are frequently used for the production of clay-polymer composites. The characterization of their thermal behavior and decomposition was carried out mainly under reduced conditions by using N₂, He or Ar gas flow.

The object of this study was to investigate the thermal decomposition of cationic (PAM_{S,t40}Cl), nonionic (PAM[°]_S), and anionic (NaPAM_{S,t40}) polyacrylamide under synthetic air (SynA) in detail using a thermogravimetry/differential scanning calorimetry (TG/DSC) system connected to a quadrupole mass spectrometer (MS). MS data indicated the release of NH₃, CH₄ and NO together with H₂O, CO₂ and NO₂ during decomposition. The gas release differed between the three polymers.

Stoichiometric calculations showed that PAM_{S,t40}Cl and PAM[°]_S decomposed completely, while NaPAM_{S,t40} decomposed only partially and the Na present for charge balancing remained in the form of Na₂O.

The thermal decomposition of PAM_{S,t40}Cl, PAM[°]_S and NaPAM_{S,t40} under SynA occurred via pyrolysis and oxidation reactions.

1. Introduction

A large number of publications exist on the preparation of clay-polymer or smectite-polyacrylamide (PAM) composites (Denoyel et al., 1990; Deng et al., 2006; Haase and Schanz, 2016). Characterization of the composites occurred qualitatively e.g. by X-ray diffraction analysis (XRD), Fourier transform infrared (FTIR) spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy. Clay-polymer or smectite-PAM composites are usually characterized quantitatively by their adsorption isotherms, which were used to determine the maximum amount of PAM that can be adsorbed on inner and outer surfaces of smectites. In contrast simultaneous thermal analysis can be applied to determine the effective PAM content in smectite-PAM composites. At the same time, information on the thermal stability of PAM and of smectite-PAM composites are available.

Tutas et al. (1987) studied the decomposition of polyacrylamide (PAM) up to 600 °C under N₂ using simultaneous thermogravimetry (TG), derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC). They detected three mass loss steps at 110, 330 and

400 °C, which are associated with three endothermic peaks but no exothermic peak was detected. They reported that the endothermic decomposition of PAM and some of its decomposition products took place in the same temperature region as the exothermic decomposition of polyacrylonitrile (PAN). They assumed a slight exothermic decomposition of PAN caused by cross-linking. They detected one weight loss of 10% at 110 °C, which is related to hydrogen bonded water in PAM. Release of NH₃ and H₂O partly from PAN structure and from the remaining PAM at about 400 °C, which is combined with a weight loss of 17%.

Leung et al. (1987) studied the decomposition of PAM and poly(acrylamide-co-acrylate) under N₂ up to 600 °C using TG-DSC. The analysis of the released gas molecules occurred separately by gas chromatography (GC)/mass spectrometry (MS). They detected two or three decomposition ranges between 200 and 500 °C for the three samples. The complete weight loss over the whole temperature range was between 36 and 66% and was combined with the release of H₂O, NH₃, CO₂, CO, N₂.

Tóth et al. (1990) studied the thermal decomposition of bentonite-PAM complexes under Ar, as compared to the behavior of PAM

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and bentonite separately, using TG-MS. They detected three thermal degradation ranges for PAM with a total mass loss of 85%. The degradation is combined with the release of H₂O, CO₂, NH₃, CO and aliphatic compounds (HCN, C₃H₃N, C₄H₆, and C₂H₅N) and the final breakdown of the PAM backbone, accompanied by charring processes was taking place above 400 °C. Their results supported the degradation mechanism proposed by Leung et al. (1987).

Van Dyke and Kasperski (1993) studied the thermal behavior of PAM heated in He atmosphere using TG in the range of 30–600 °C. The evolved gases were monitored by FTIR. They detected two weight loss steps between 220–340 °C and 340–440 °C. In the first decomposition stage H₂O, NH₃ and small amount of CO₂ were released and the reactions occurred only on the pendant amide groups. In the second decomposition stage, imides break down to form nitrile groups, and CO₂ was released. Simultaneously, the main chain breakdown took place in the second stage and accounted for a large portion of the weight loss in PAM. The main chain breakdown released large amounts of glutarimide and substituted glutarimides (saturated and unsaturated).

E Silva et al. (2000) synthesized PAM and N-alkyl substituted derivatives and investigated the substances with TG in N₂ atmosphere. They investigated the glass transition temperature of PAM and the N-alkyl substituted derivatives. The glass transitions temperature decreased with increasing N-alkyl groups and was strongly influenced by polymer-polymer interactions such as hydrogen bonds. They detected that PAM decomposed in three steps.

The characterization of the thermal decomposition of polymers were carried out mainly by TG methods combined with gas analysis under N₂, Ar or He. The decomposition of PAM under streaming synthetic air (SynA) is important since the production and application of PAM and smectite-PAM composites takes place under normal laboratory conditions.

The aim of the present study is to show in detail the differences in thermal decomposition of cationic (PAM⁺_{S,τ40}), nonionic (PAM⁰_S) and anionic (PAM⁻_{S,τ40}) polyacrylamide (PAMs) under SynA using MS data showing gas release during STA.

2. Material

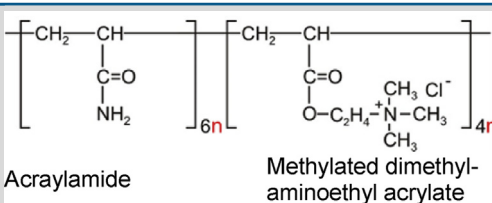
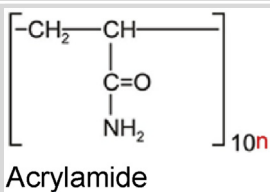
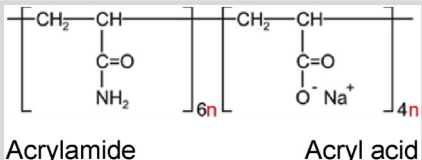
Three commercial cationic (PAM⁺_{S,τ40}), nonionic (PAM⁰_S) and anionic (PAM⁻_{S,τ40}) polyacrylamides (PAMs) with a medium chain length produced by the SNF group (Andrézieux, France) were used (Table 1). PAM⁺_{S,τ40} and PAM⁻_{S,τ40} have a charge density of 40%. The positive and negative charge of PAM⁺_{S,τ40} and PAM⁻_{S,τ40} was balanced by Cl⁻ and Na⁺, respectively.

A raw kaolin KBE-1 (98% kaolinite) from a deposit in Germany supplied by Amberger Kaolinwerke Eduard Kick GmbH & Co. KG (Hirschau, Germany) was used to produce a metakaolinite (Metakln). The kaolin KBE-1 was heated to 1000 °C in an oven. Metakln was used as an inert material to prevent PAM from creeping out of the crucible during STA measurement. Six different physical mixtures were prepared by mixing the Metakln with PAM⁺_{S,τ40}, PAM⁰_S and PAM⁻_{S,τ40} in an agate mortar to investigate the decomposition behavior of the three PAMs. The concentration of each PAM in the physical mixture was 10 and 20%. All samples were stored over a saturated solution of Mg(NO₃)₂ in a desiccator to equilibrate at a relative humidity of 53%.

3. Methods

STA 449 C Jupiter with a thermogravimetry/differential scanning calorimetry (TG/DSC) sample holder (Netzsch-Gerätebau GmbH, Selb, Germany) with a quadrupole mass spectrometer (MS) 403 C Aëolos (InProcess Instruments (IPI)/NETZSCH-Gerätebau GmbH, Selb, Germany) coupling, which is connected by a heated quartz glass capillary (T = 230 °C) was used to investigate the thermal behavior of the samples. The following measurement conditions were applied: heating rate 10 K/min, temperature range 35–1100 °C, streaming synthetic air (SynA: 79 mass-% N₂/21 mass-% O₂; 50 mL min⁻¹) as purge gas and 20 mL min⁻¹ N₂ as protective gas. An empty Pt/Rh crucible (diameter 5 mm and height 5 mm) with a punched lid was used as inert reference sample and sample weight was 60–105 mg. An isothermal segment at 35 °C was placed prior to the dynamic segment for 10 min to restore the atmospheric equilibrium in the furnace chamber. The isothermal segment resulted in a low

Table 1. Structural formula and molar weight of PAMs.

Polymer	Monomer units	M Oligomer with n = 1 [g/mol]	M commercial polymer [g/mol]
PAM ⁺ _{S,τ40} Na	 <p>Acrylamide</p> <p>Methylated dimethyl-aminoethyl acrylate</p>	1200	7.0–9.5 × 10 ⁶ n = 6–8 × 10 ³
PAM ⁰ _S	 <p>Acrylamide</p>	710	10 × 10 ⁶ n = 14 × 10 ³
NaPAM ⁻ _{S,τ40}	 <p>Acrylamide</p> <p>Acryl acid</p>	802	14–17 × 10 ⁶ n = 17.5–21 × 10 ³

mass loss indicated by the starting mass of the dynamic segment. The mass loss was determined from the TG curve. The first derivation of the TG curve (DTG) was used to resolve overlapping reactions associated with mass loss. The gas release was detected by MS. The following mass fragment numbers $m/z = 12, 13, 14, 15, 16, 17, 18, 28, 29, 30, 35, 36, 44, 46, 64$ were selected. Table 2 shows the mass fragments of typical gas molecules of organic matter (70 eV; Emmerich, 2011; NIST, 2008).

4. Results and discussion

The STA measurement of MetakIn showed a small mass loss of 0.43% over the entire temperature range. The MS curves of $m/z = 18$ and $m/z = 44$ showed a small release of H_2O and CO_2 up to 600 °C.

The TG curve of $PAM_{S,\tau40}Cl$ (Figure 1) and PAM°_S (Figure 2) showed two mass losses. The first occurred in the range between 35 and 200 °C, while the second one occurred between 200 and 700 °C. The DTG curve indicated three mass loss steps (Table 3). The TG curve of $NaPAM_{S,\tau40}$ showed three mass losses (Figure 3). The first two mass losses were in the same temperature range as for the other two PAMs. The third mass loss occurred in the range between 700 and 1100 °C. According to the DTG curve, the second mass loss can be divided in two mass losses (Table 3).

The first mass loss in the region between 35 and 200 °C was linked to the release of H_2O for all three PAMs (Figures 4, 5, and 6). The second mass loss reflected the decomposition of the PAMs. The decomposition started at 200 °C with an endothermic reaction, followed by various exothermic reactions up to 650 °C (Figures 1, 2, and 3). The DSC curve of $NaPAM_{S,\tau40}$ revealed a further endothermic peak with a temperature maximum at 849 °C (Figure 3).

Between 200 and 700 °C, the DTG curve showed four, five, and five peak maxima for $PAM_{S,\tau40}Cl$, PAM°_S , and $NaPAM_{S,\tau40}$, respectively (Figures 1, 2, and 3). These endothermic and exothermic reactions were associated with maxima in the different MS curves (Figures 4, 5, and 6).

From the MS data of $m/z = 18$ and $m/z = 17$ it can be seen that the H_2O release occurred over the whole decomposition range for all three PAMs (Figures 4a-6a).

The endothermic reaction of $PAM_{S,\tau40}Cl$ was associated with the release of CH_4 ($T_{max} = 275$ °C), Cl_2/HCl ($T_{max} = 275$ °C), NO ($T_{max} = 278$ °C) and NO_2 ($T_{max} = 300$ °C). The release of CH_4 was proved by peaks in the MS curve of $m/z = 15$ and $m/z = 13$ (Figure 4c). The release of Cl_2/HCl was proved by $m/z = 35, 36$ (Figure 4d). The release of NO was proved by peaks in the MS curve of $m/z = 30$ and no peak in the curve of $m/z = 46$ (Figure 4e). The release of NO_2 is proved by $m/z = 30, 46$ (Figure 4e). The exothermic peaks in the DSC curve of $PAM_{S,\tau40}Cl$ were mainly associated with CO_2 and NO release (Figure 4e). The release of CO_2 was confirmed by the MS curve of $m/z = 44$ (Figure 4e). Between 350 and 650 °C, the curves of $m/z = 44$ and $m/z = 46$ were identical,

Table 2. Mass fragments of typical gas molecules (70 eV; Emmerich, 2011; NIST, 2008).

m/z	H_2O	CO_2	CH_4	NH_3	NO	NO_2	Cl_2	SO_2
12		x	x					
13			x					
14			x	x	x	x		
15			x	x	x			
16	x		x	x	x	x		
17	x			x				
18	x			x				
30					x	x		
35							x	
36							x	
44		x						
46		x				x		
64								x

Main mass fragment are highlighted in bold.

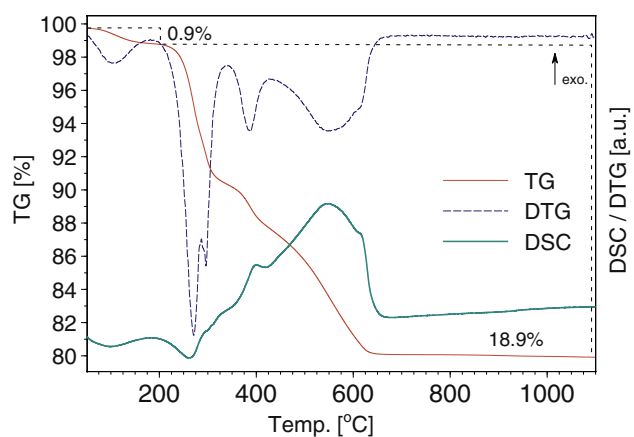


Figure 1. Thermal analysis of $PAM_{S,\tau40}Cl$ (20%; starting mass: 99.73%).

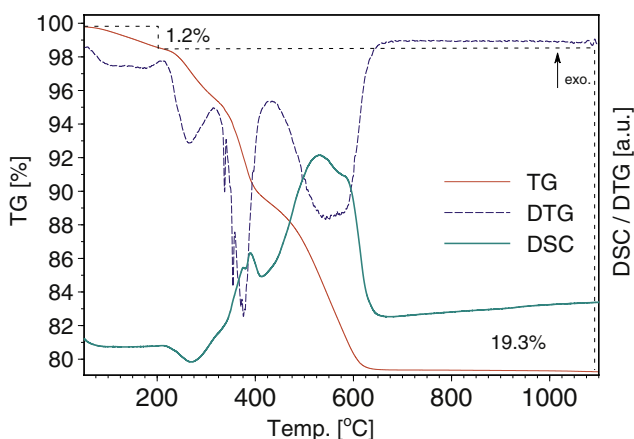


Figure 2. Thermal analysis of PAM°_S (20%; starting mass: 99.81%).

Table 3. Mass loss of the three PAMs (20%).

Sample	$PAM_{S,\tau40}Cl$	PAM°_S	$NaPAM_{S,\tau40}$
Starting mass of TG [%]	99.73	99.81	99.84
Δm_1 [%]	0.9	1.2	1.3
Δm_2 [%]	18.9	19.3	15.4
$\Delta m_{2,1}$ [%]	8.5	3.0	6.0
$\Delta m_{2,2}$ [%]	2.6	6.5	9.4
$\Delta m_{2,3}$ [%]	7.8	9.8	
Δm_3 [%]	-	-	1.1

Intermediated values. Italics used for easier reading.

which means that there was no release of NO_2 in this temperature range (Figure 4e). The MS curve of $m/z = 30$ indicated the release of NO between 350 and 650 °C (Figure 4e).

The endothermic reaction of PAM°_S was associated with the release of CH_4 and NH_3 ($T_{max} = 273$ °C) and NO ($T_{max} = 272$ °C), which was proved by the MS curves of $m/z = 17$ (Figure 5b), $m/z = 15$ (Figure 5b) and $m/z = 30$ (Figure 5d), respectively. Both, NH_3 and CH_4 were released, because the peak ratios within the two MS curves differed significantly between 200 and 400 °C (Figure 5b). The release of NH_3 (Figure 5b) also occurred at elevated temperatures (374 °C and 481 °C). The exothermic reactions of PAM°_S were associated with the release of NO and CO_2 (Figure 5d). The MS data showed no release of NO_2 (Figure 5d). The MS curves of $m/z = 44$ and $m/z = 46$ were identical (Figure 5d).

The MS curve of $m/z = 64$ of $PAM_{S,\tau40}Cl$ (Figure 4b) and PAM°_S (Figure 5c) showed the release of SO_2 , which might be a residual from

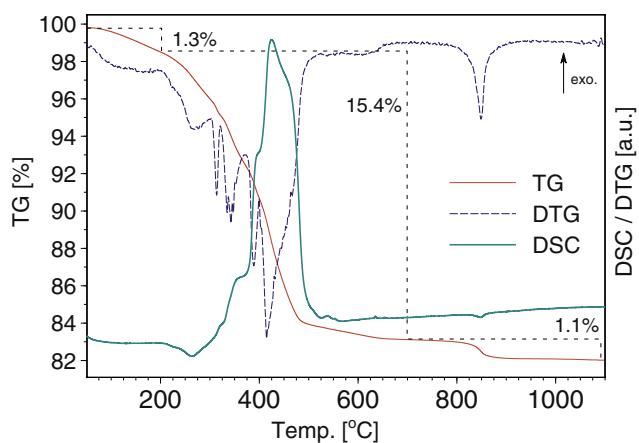


Figure 3. Thermal analysis of NaPAM_{S,τ40} (20%; starting mass: 99.84%).

production. Sulphuric acid decomposed between 300 and 450 °C (Schwartz et al., 2000).

The endothermic reaction of NaPAM_{S,τ40} was associated with the release of NH₃ (T_{max} = 279 °C, Figure 6b) and NO (T_{max} = 291 °C,

Figure 6c). The release of both gases occurs even at higher temperatures. The release was completed up to 450 °C (Figure 6b, c). While decomposing NaPAM_{S,τ40}, no NO₂ (Figure 6c) and no CH₄ (Figure 6b) were released. The MS curves of m/z = 44 and m/z = 46 were identical, they confirmed the release of CO₂ (Figure 6c). Also the endothermic reaction at 849 °C was associated with a CO₂ release (Figure 6c). This suggests that the Na used for charge balancing reacted with CO₂ to form Na₂CO₃, which decomposed to Na₂O at higher temperatures under CO₂ release (Figure 6c).

Comparison of the theoretical and measured mass losses revealed, that PAM_{S,τ40}Cl and PAM_S decomposed completely (Table 4). The mass loss of the Metakln has been taken into account in the calculation.

The decomposition of PAM_{S,τ40} is more complex. The Na₂O content in the residue deviates strongly from the theoretically calculated Na₂O content (Table 5). One possible reason is that the actual charge density is higher than the specified charge density (Table 6). Another possible explanation could be that a small part of the sodium was already expelled at higher temperatures.

The calculations revealed that NaPAM_{S,τ40} decomposed partly, according to the following equation of reaction:

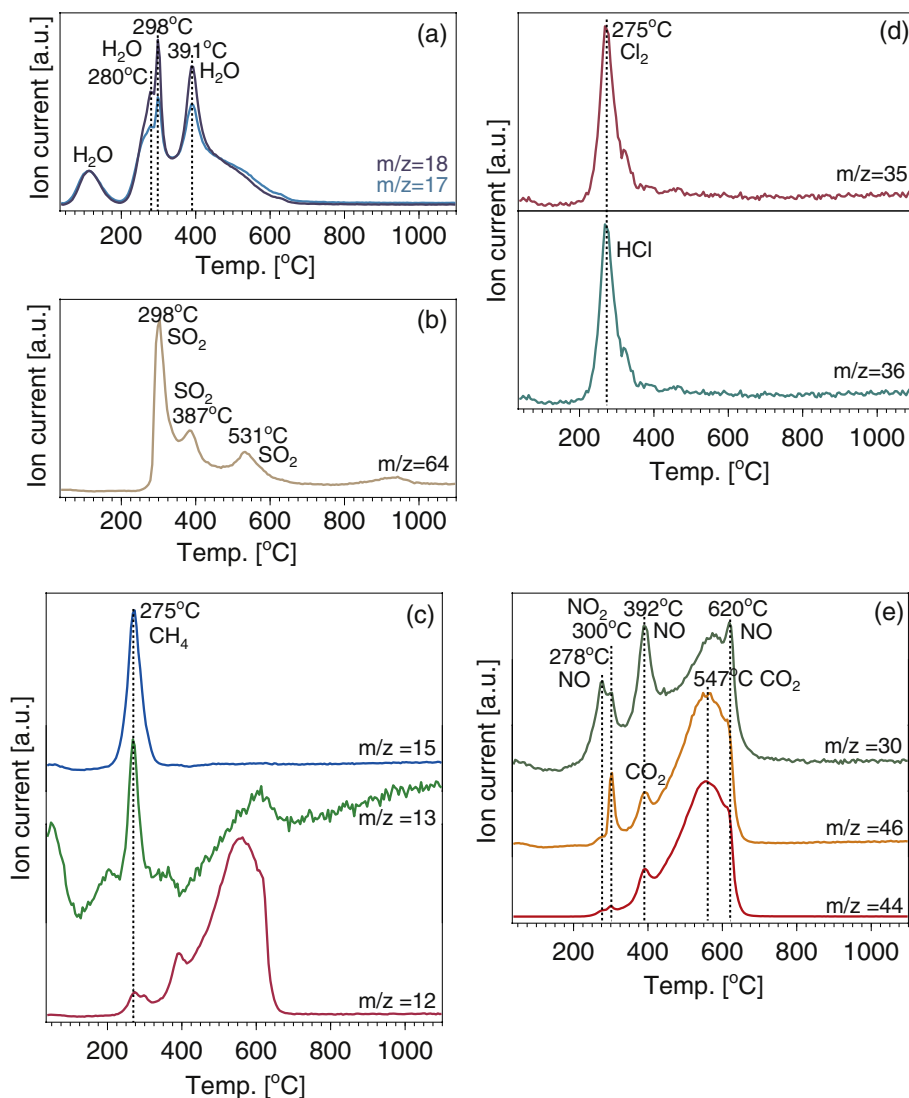


Figure 4. MS data of PAM_{S,τ40}Cl a) m/z = 17, 18; b) m/z = 64; c) m/z = 12, 13, 15; d) m/z = 35, 36 and e) m/z = 30, 44, 46; (starting temperature of MS spectra: 35 °C).

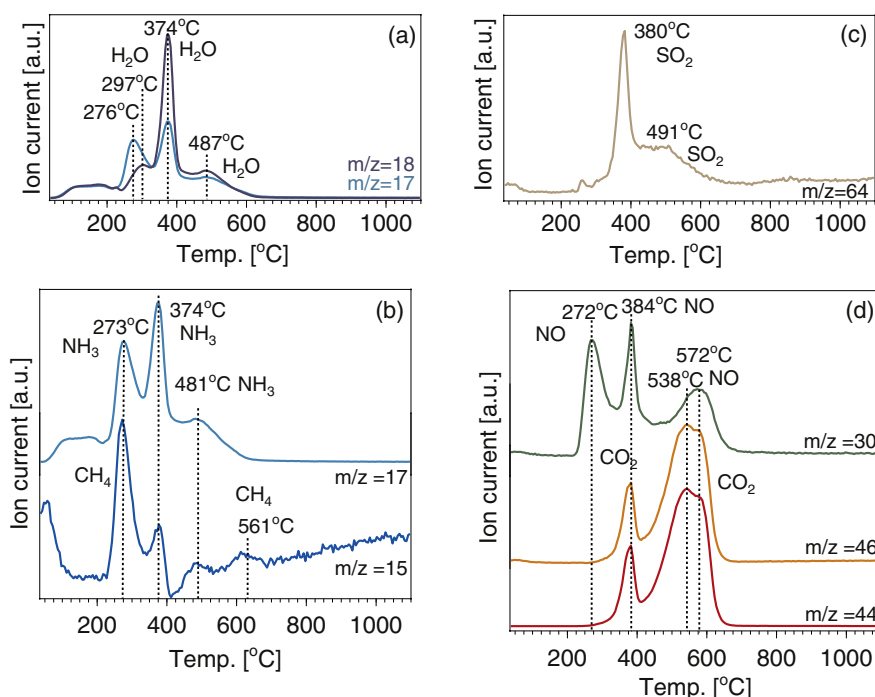


Figure 5. MS data of PAM^s a) m/z = 17, 18; b) m/z = 15, 17; c) m/z = 64; d) and d) m/z = 30, 44, 46; (starting temperature of MS spectra: 35 °C).

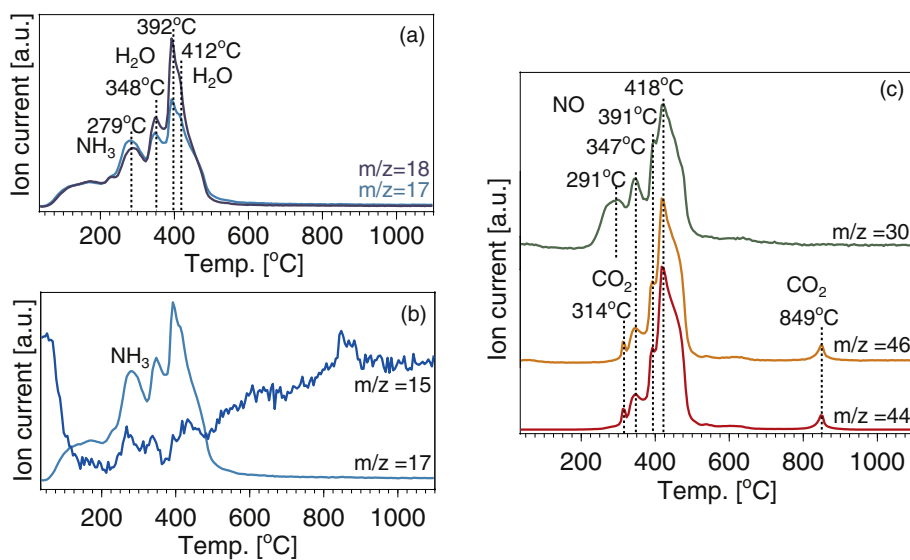


Figure 6. MS data of NaPAM_{s,t40} a) m/z = 17, 18; b) m/z = 64 and c) m/z = 30, 44, 46; (starting temperature of MS spectra: 35 °C).

Table 4. Calculated mass loss compared with the measured mass loss, reflecting the amount of the polymer.

m_{total} [mg]	Amount PAM [%]	$m_{\text{calc. Metaklin}}$ [mg]	$m_{\text{calc. PAM}}$ [mg]	$\Delta m_{\text{calc. Metaklin}}$ [mg]	$\Delta m_{\text{total calc}}$ [mg]	$\Delta m_{\text{total TG}}$ [mg]	$\Delta m_{\text{polymer}}$ [mg]	$\Delta m_{\text{polymer}}$ [%]	deviation
PAM _{s,t40} Cl									
61.266	10	55.139	6.127	0.237	6.364	6.73	6.493	10.6	5.4
98.281	20	78.625	19.656	0.338	19.994	19.64	19.302	19.6	1.8
PAM ^s									
87.757	10	78.981	8.776	0.339	9.115	8.72	8.381	9.6	4.3
100.664	20	80.531	20.133	0.346	20.479	20.89	20.544	20.4	2

Table 5. Calculated Na₂O quantity based on the theoretical values compared to the quantity based on the measured data.

m _{total} [mg]	Amount PAM [%]	m _{calc, Metakln} [mg]	m _{calc, PAM} [mg]	m _{dry-Metakln} [mg]	m _{Na2O} [mg]	m _{residual} [mg]	Δm _{TG} [mg]	m _{residual-TG} [mg]	m _{Na2O, TG} [mg]
NaPAM _{S,τ40}									
97.399	10	87.659	9.74	87.283	1.51	88.793	7.975	89.424	2.14
81.134	20	64.907	16.227	64.628	2.52	67.143	13.582	67.552	2.92

The main results are highlighted in bold for easier reading.

Table 6. Influence of charge density on the calculated Na₂O quantity (NaPAM_{S,τ40}, 20%).

Charge density	ratio Acrylamide: Acrylic acid	Na [mol]	Na ₂ O [mol]	m _{Na2O} [%]	m _{Na2O} [mg]	m _{Na2O, TG} [mg]	deviation
40	6 : 4	4	2	15.5	2.52	2.92	14
35	13 : 7	7	3.5	13.7	2.22	2.92	24
45	11 : 9	9	4.5	17.2	2.78	2.92	5
50	5 : 5	5	2.5	18.8	3.05	2.92	4

The main results are highlighted in bold for easier reading.

5. Conclusions

The thermal decomposition of PAM_{S,τ40}Cl, PAM^o_S, and NaPAM_{S,τ40} under SynA was investigated in detail using a TG/DSC system coupled with MS. Decomposition of PAMs is very complex and does not simply result in CO₂, H₂O and NO₂. Decomposition of PAM_{S,τ40}Cl, PAM^o_S and NaPAM_{S,τ40} takes place in several stages by pyrolytic decomposition and oxidation, with both processes overlapping each other or running parallel. MS data indicated the additional release of NH₃, CH₄ and NO together with H₂O, CO₂ and NO₂.

The gas release differed between the three investigated polymers. Stoichiometric calculations showed that PAM_{S,τ40}Cl and PAM^o_S decomposed completely, while NaPAM_{S,τ40} decomposed only partially and the Na present for charge balancing remained in the form of Na₂O.

Declarations

Author contribution statement

Annett Steudel: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Frank Friedrich: Conceived and designed the experiments; Analyzed and interpreted the data.

Wolfgang Lieske & Diethard König: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Wiebke Baille & Rainer Schuhmann: Analyzed and interpreted the data.

Katja Ememrich: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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