

Thermal decomposition of acrylamide from polyacrylamide

Time-resolved pyrolysis with ion-attachment mass spectrometry

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Abstract Ion-attachment mass spectrometry with a temperature-programmed direct probe allows the detection of intact pyrolysis products. It, therefore, offers the opportunity to monitor directly thermal byproducts on a real-time basis and potentially to detect thermally unstable products. With this technique, we investigated the thermal decomposition of polyacrylamide (PAA). Pyrolysis of PAA at around 450 °C produces many products (e.g., amides, imides, nitriles, ketones, aldehydes, and acrylamide oligomers). Acrylamide, which is a possible carcinogen, is produced abundantly in various industries, and, therefore, continues to be a cause for concern. We also investigated the kinetics of the thermal decomposition of PAA, and observed that the degradation of acrylamide obeys Arrhenius kinetics, which allowed us to correlate the rate constant with the absolute temperature and the activation energy. The activation energy of thermal decomposition was calculated from selected ion-monitoring curves of acrylamide.

Keywords Thermal decomposition · Acrylamide · Polyacrylamide · Ion-attachment mass spectrometry · Time-resolved pyrolysis

Introduction

The thermal decomposition of polyacrylamide (PAA) has received continued attention in the literature [1–5] for the

following reasons: (i) PAA is used as an important thermoplastic material in many industries; (ii) the acrylamide monomer, which is a neurotoxin and carcinogen, can be present in small amounts in polymerized acrylamide; and (iii) PAA used in the food industry may contaminate food with acrylamide. Thermal decomposition of PAA under certain conditions has been reported to cause the release of acrylamide [4], and at cooking temperatures, degradation reactions are likely to occur [5]. Therefore, a thorough understanding of its thermal behavior is of crucial importance for end-use applications.

PAA polymers have been studied by means of thermogravimetric analysis [6–8], liquid chromatography [9], ¹³C nuclear magnetic resonance spectroscopy [7], infrared spectroscopy [6], and mass spectrometry [6, 7, 10]. These studies revealed that pyrolysis–gas chromatography/electron impact mass spectrometry is effective for the rapid analysis of polymers with only small amounts of sample and minimal sample preparation.

The evolved gas analysis–mass spectrometry (EGA–MS) method has been studied extensively [6, 7] and found to be useful for the characterization of thermal decomposition processes. In addition to the standard mass spectra, spectra obtained by means of total ion monitoring or selected ion monitoring at various temperatures provide useful information for kinetic studies of thermal decomposition processes. However, only a few reports about acrylamide production [10, 11] or the thermo-oxidative behavior [12] and kinetics of acrylamide decomposition [8] have appeared in the literature. This information is essential to understand the thermal decomposition properties of PAA materials during their thermal destruction. However, interpretation of electron impact mass spectra is complicated by the molecular fragmentation, and the electron

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impact mass spectra of PAA show many different fragmentation ions [13].

Recently, we developed, extensively tested, and optimized a novel technique based on Li^+ ion-attachment mass spectrometry (IAMS) [14–16]. One advantage of this efficient, sensitive technique is that it can be used to analyze gaseous compounds directly, because the mass spectra contain only peaks for quasi-molecular ions formed by Li^+ attachment to the chemical species, including free radicals. We anticipated that the coupling of EGA and IAMS [17–19] would work well for the analysis of a wide variety of polymers, because the simplicity of ion-attachment spectra permits the analysis of mixtures whose electron impact spectra would otherwise be difficult to interpret.

Here, we used EGA–IAMS to analyze PAA. We identified and classified the thermal decomposition products of PAA by analyzing the mass spectra of degraded samples. In addition, we analyzed the kinetics of acrylamide release from PAA during heating.

Experimental

Apparatus

Experiments were performed with an ion-attachment mass spectrometer (Canon ANELVA Corp., Kawasaki, Japan) for a quadrupole mass spectrometer with a Li^+ ion emitter and a homemade direct inlet probe (DIP) for EGA [17]. This EGA probe allows the direct insertion of the solid polymer sample, which is then heated to evaporation in a buffer gas. Time-resolved pyrolysis mass spectra were obtained under ion-attachment (IA) ionization conditions. The mass range was extended to m/z 400. IAMS provides a measure of mass as a guide to product identity, because it provides only the molecular ions for each product species [14–19].

EGA probe and procedure

A detailed description of the EGA probe setup has been provided elsewhere [17]; however, we will briefly review the main points. Samples are pyrolyzed via the direct inlet probe, and the programmed temperature is increased by heating the probe from 50 to 500 °C at a rate of 20 °C min^{-1} . The temperature is then held at 500 °C for 10 min. The pyrolysis products formed are ionized and then detected. The advantage of this technique is that the degradation occurs close to the ion source, and hence primary degradation products may be observed by this technique, compared with conventional pyrolysis–GC/MS (Py–GC/MS).

Apparent activation energies for decomposition of acrylamide

EGA–IAMS can also be used as a temperature-programmed reactor for non-isothermal kinetic studies. In addition to the standard mass spectra, plots of mass signals [in total ion monitor (TIM) and selected ion monitor (SIM) mode] against temperature, can be obtained. These plots, referred to as a thermograms or pyrograms, have been used to construct decomposition profiles. Kinetic parameters can be calculated from the simple Arrhenius equation, and the apparent activation energy (E_a) can also be calculated [20]. Mass spectral data collected by means of SIM serve as a basis for these calculations. We used the SIM mode for thermal behavior evaluations of targeted species of acrylamide. The ionic signal (i) acquired from the real-time SIM of acrylamide-based chemicals released from the thermal decomposition of PAA was used to obtain the functional form of the kinetic rate expression.

Sample and sampling

Standard PAA homopolymers with MWs of 9×10^5 and $4 \times 10^6 \text{ g mol}^{-1}$ were obtained from the Aldrich Chemical Company (Tokyo, Japan). In EGA experiments, 2 mg samples were used. A small slice or portion of polymer was placed into a titanium crucible and introduced into the instrument via the direct probe.

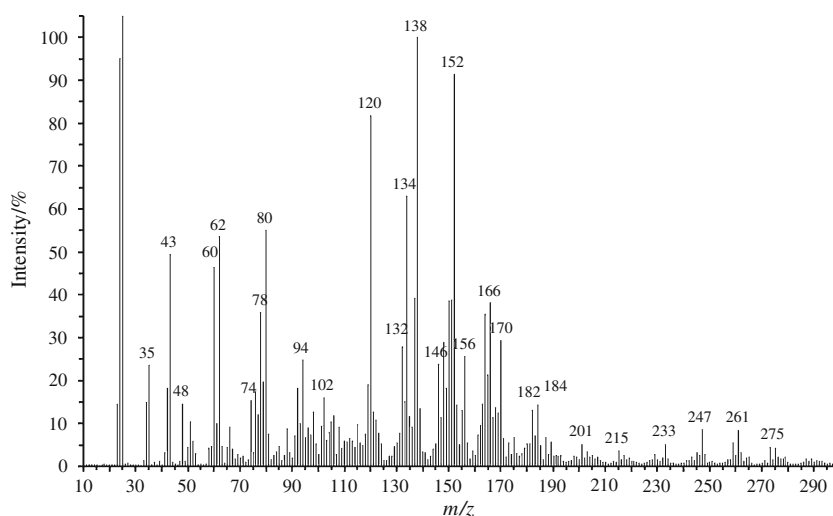
Results and discussion

Identification of pyrolysis products

Evolution profiles of thermal products during pyrolysis of PAA, shown by the time dependence of the ion signals in the TIM mode, indicated that thermal decomposition started at above 350 °C with the product gas emissions in one step. Typical mass spectra obtained by thermal decomposition of samples at 450 °C are shown in Fig. 1. The relative intensities of the mass peaks were normalized to 100 U for the highest peak among the species produced during pyrolysis (i.e., $\text{C}_7\text{H}_{17}\text{NO Li}^+$, m/z 138). The peaks observed in the spectra are directly related to the thermal decomposition products because IAMS provides peaks only for the molecular ions of the products.

Structural assignments for the mass spectra peaks are shown in Table 1 and are based on the formulae and relative intensities of the mass peaks of the pyrolysis products. The peaks were assigned principally on the basis of mass number, and therefore the assignments are not without ambiguity. For example, the aldehyde peaks by the formula $\text{C}_n\text{H}_{2n+1}\text{CHO}$ are isobaric with the ketone peaks.

Fig. 1 A typical Li^+ -adduct mass spectrum of the products from the pyrolysis of polyacrylamide (PAA) in nitrogen, recorded at an evolved gas analysis (EGA) probe temperature of 250 °C. Samples were placed in the EGA probe and then heated linearly from room temperature to 500 °C at a programmed rate of 20 °C min^{-1} . The relative intensities of the mass peaks were normalized to 100 U for the highest peak among the species produced in the pyrolysis process ($\text{C}_7\text{H}_{17}\text{NOLi}^+$, m/z 138)



Given the chemical structure of acrylamide, which is the monomer of PAA, and the fact that in this system isobaric products are indistinguishable, we speculated that both aldehydes and ketones were formed.

Classification of decomposition products

Many researchers have analyzed the thermal decomposition of PAA [6–12]. In their studies, all product species were broadly classified as amides, imides, nitriles, ketones, aldehydes, and acrylamide oligomers. Here, we observed a similar trend with respect to the nature of the thermal decomposition products and classified them into groups based on the alkyl radical for amides, imides, nitriles, and aldehydes, except for NH_3 , H_2O , CO , CO_2 , ketones, and acrylamide oligomers (Table 2). The detection of each chemical species produced during the thermal process is briefly described below.

Amides Considerable quantities of amide species, such as $\text{C}_n\text{H}_{2n+1}\text{CONH}_2$ and $\text{C}_n\text{H}_{2n-1}\text{CONH}_2$, were produced during the thermal decomposition reactions; the presence of substantial amounts of species with n values up to 9 is shown (Table 2). This observation correlates qualitatively with the simple thermal cleavage of the straight chain in PAA.

The Li^+ -adduct mass spectrum clearly shows peaks at m/z 78 and 151 among the many amide peaks, indicating the formation of acrylamide and the acrylamide oligomer $\text{H}(\text{C}_n\text{H}_{2n+1}\text{CONH}_2)_2\text{H}$, respectively. Our EGA–IAMS system clearly identifies products at an intermediate time window on a real-time analysis basis. It should be noted that EGA–IAMS appears to allow the observation of species that form during the primary thermal degradation process.

Nitriles The nitrile group was detected. The Li^+ -adduct mass spectrum clearly showed peaks at m/z 34, 48, 62, 76, 132, 146, and 60, 74, 102, suggesting that $\text{C}_n\text{H}_{2n+1}\text{CN}$ ($n = 0–3, 7, 8$) and $\text{C}_n\text{H}_{2n-1}\text{CN}$ ($n = 2, 3, 5$), were produced. The relative peak intensity of $\text{C}_2\text{H}_5\text{CN}$ was the highest. This observation correlates qualitatively with H_2O elimination from the CO–NH_2 groups in PAA. Moreover, these observations are consistent with the fact that a sizeable peak was present at m/z 18. The detected species (m/z 34) may be the ionic form of the Li^+ -adduct HCN , a well-known toxic compound that is produced during the pyrolysis of PAA [21]. This result indicates that well-known toxic substances can be produced during incineration or plasma decomposition of PAA. Hence, we suggest that remediation is required to prevent such end products from escaping into the atmosphere.

$\text{C}_n\text{H}_{2n}\text{O}$, $\text{C}_n\text{H}_{2n+2}\text{O}$, and $\text{C}_n\text{H}_{2n-2}\text{O}$ Thermal decomposition products with formulas of $\text{C}_n\text{H}_{2n}\text{O}$, $\text{C}_n\text{H}_{2n+2}\text{O}$, and $\text{C}_n\text{H}_{2n-2}\text{O}$ were observed. These product species of $\text{C}_n\text{H}_{2n}\text{O}$ can be classified as aldehydes or ketones with the general formula $\text{C}_n\text{H}_{2n+1}\text{CHO}$ or R_nCOR_m , ($\text{R}_n, \text{R}_m =$ alkyl radicals), whereas the $\text{C}_n\text{H}_{2n+2}\text{O}$ species can be classified as alcohols or ethers with the general formula $\text{C}_n\text{H}_{2n+1}\text{OH}$ or R_nOR_n . Both products can arise during the pyrolysis, according to the literature [6, 7, 10]; however, in this study, they were indistinguishable.

$\text{C}_n\text{H}_{2n-1}\text{NO}$, $\text{C}_n\text{H}_{2n+1}\text{NO}$, $\text{C}_n\text{H}_{2n+3}\text{NO}$, $\text{C}_n\text{H}_{2n-3}\text{NO}_2$, $\text{C}_n\text{H}_{2n+1}\text{NO}_3$, $\text{C}_n\text{H}_{2n+3}\text{NO}_3$, and $\text{C}_n\text{H}_{2n+4}\text{N}_2\text{O}_2$ We detected many N-containing homologous compounds with single and double bonds. These species have the general compositional formulas $\text{C}_n\text{H}_{2n-1}\text{NO}$ ($n = 3–8$), and $\text{C}_n\text{H}_{2n+1}\text{NO}$ ($n = 3, 4, 6, 8, 9$), $\text{C}_n\text{H}_{2n+3}\text{NO}$, and $\text{C}_n\text{H}_{2n-3}\text{NO}_2$. Possible structures are listed in Table 2. $\text{C}_n\text{H}_{2n-3}\text{NO}_2$ suggests the formation of glutarimide homologs [6].

Table 1 Assignments of mass spectral peaks and the relative intensities of the possible products formed from polyacrylamide in a nitrogen environment

<i>m/z</i>	Product	Intensity/%
24	NH ₃	95
25	H ₂ O	294
34	HCN	15
35	N ₂ , CO	24
42	NH ₃ + H ₂ O	18
43	(H ₂ O) ₂	49
48	CH ₃ CN	15
51	CH ₃ CHO, CO ₂	11
60	C ₂ H ₃ CN	46
62	C ₂ H ₅ CN	54
74	C ₃ H ₅ CN	16
76	C ₃ H ₇ CN	17
77	C ₄ H ₆ O	12
78	C ₂ H ₃ CONH ₂	36
79	C ₃ H ₇ CHO	20
80	C ₂ H ₅ CONH ₂	55
92	C ₃ H ₅ CONH ₂ , C ₃ H ₃ NO ₂	18
93	C ₃ H ₉ CHO	10
94	C ₃ H ₇ CONH ₂	25
98	C ₂ H ₅ NO ₃	13
102	C ₅ H ₉ CN	16
105	C ₆ H ₁₀ O	10
106	C ₄ H ₇ CONH ₂ , C ₄ H ₅ NO ₂	12
119	C ₇ H ₁₂ O	19
120	C ₅ H ₉ CONH ₂ , C ₅ H ₇ NO ₂	82
121	C ₆ H ₁₃ CHO	13
122	C ₅ H ₁₁ CONH ₂	11
132	C ₇ H ₁₅ CN	28
133	C ₈ H ₁₄ O	15
134	C ₆ H ₁₁ CONH ₂ , C ₆ H ₉ NO ₂	63
135	C ₇ H ₁₅ CHO	12
137	C ₈ H ₁₈ O	39
138	C ₇ H ₁₇ NO	100
146	C ₈ H ₁₇ CN	24
147	C ₆ H ₁₆ O	11
148	C ₇ H ₁₃ CONH ₂ , C ₇ H ₁₁ NO ₂	29
149	C ₈ H ₁₇ CHO	18
150	C ₇ H ₁₅ CONH ₂	39
151	H(C ₂ H ₃ CONH ₂) ₂ H, C ₉ H ₂₀ O	39
152	C ₈ H ₁₉ NO	92
155	C ₆ H ₁₆ N ₂ O ₂	13
156	C ₆ H ₁₅ NO ₃	26
163	C ₉ H ₁₉ CHO	15
164	C ₈ H ₁₇ CONH ₂	35
165	C ₁₀ H ₂₂ O	21
166	C ₉ H ₂₁ NO	38
168	C ₇ H ₁₅ NO ₃	14

Table 1 continued

<i>m/z</i>	Product	Intensity/%
169	C ₇ H ₁₈ N ₂ O ₂	12
170	C ₇ H ₁₇ NO ₃	29
182	C ₈ H ₁₇ NO ₃	13
184	C ₈ H ₁₉ NO ₃	14

Intensities of monoisotopic species are reported. The relative intensities of the mass peaks were normalized to 100 U for the C₇H₁₇NOLi⁺ peak. Only peaks with relative intensities of more than 10 % are shown. *m/z* values are given for the Li⁺ adduct

As stated earlier, for the assignment of mass spectral peaks, validity was based principally on mass number. As C_{*n*}H_{2*n*-1}NO compound peaks are isobaric with the C_{*n*}H_{2*n*-3}NO₂ group peaks, they could not be distinguished from each other. Because of PAA's chemical structure, we tentatively speculated that both compounds were formed.

Comparison with previous work

Although there are similarities between our results and the published literature, we did observe some differences. In particular, the abundance distribution of the decomposed products was different; in general, we detected lighter species. EGA indicated the formation of small molecular stable compounds. The appearance of peaks corresponding to *m/z* 24, 25, 34, 35, 51, and 78 was present, indicating that NH₃, H₂O, HCN, CO, CO₂, and acrylamide (monomer) were produced.

Many research groups have also investigated the thermal decomposition mechanism of PAA [6, 7, 21]. During the pyrolysis process, random decomposition, via breaks in the main polymer chain (polymer scission), occurs initially at heated temperature, yields monomer, oligomer, or chain fragments, and is then usually followed by a sequence of complicated chemical processes, such as intermolecular and intramolecular rearrangement, elimination, hydration, and abstraction. Although we did not perform a quantitative assessment or rigorous analysis of the degradation mechanism in this study, our results are essentially consistent with the reported data for PAA thermal degradation.

The kinetics of PAA pyrolysis

By selecting the specific ion chromatogram of *m/z* 78 and following it over the entire reaction temperature range, the evolution profile of the corresponding acrylamide during decomposition can be seen in the inset of Fig. 2. The peak at *m/z* 78 appeared at 350 °C, increased to a maximum at 430 °C, and then almost disappeared at around 530 °C. Figure 2 also illustrates the TIM profiles of all of the decomposed species, indicating that thermal decomposition started at above 350 °C.

Table 2 Analysis of the products of pyrolysis of polyacrylamide

Type	$n = 0$	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$	$n = 9$	$n = 10$
Nitrile $C_nH_{2n+1}CN$	HCN 15 %	CH_3CN 15 %	C_2H_5CN 54 %	C_3H_7CN 17 %				$C_7H_{15}CN$ 28 %	$C_8H_{17}CN$ 24 %		
Nitrile $_nH_{2n-1}CN$			C_2H_3CN 46 %	C_3H_5CN 16 %		C_3H_9CN 16 %					
Aldehyde $C_nH_{2n+1}CHO$		CH_3CHO 11 %		C_3H_7CHO 20 %	C_3H_9CHO 10 %		$C_6H_{13}CHO$ 13 %	$C_7H_{15}CHO$ 12 %	$C_8H_{17}CHO$ 18 %	$C_9H_{19}CHO$ 15 %	$C_{10}H_{22}O$ 21 %
Alcohol or Ether $C_nH_{2n+2}O$											
Amide, R-CONH ₂ $C_nH_{2n-1}NO$				$C_2H_3CONH_2$ 36 %	$C_3H_5CONH_2$ 18 %	$C_4H_7CONH_2$ 12 %	$C_5H_9CONH_2$ 82 % (12 %)	$C_6H_{11CONH_2}$ 63 %	$C_7H_{13CONH_2}$ 29 %	$C_8H_{15CONH_2}$ 29 %	$C_9H_{17CONH_2}$ 35 %
Amide, R-CONH ₂ $C_nH_{2n+1}NO$				$C_2H_5CONH_2$ 55 %	$C_3H_7CONH_2$ 25 %	$C_4H_9CONH_2$ 12 %	$C_5H_{11CONH_2}$ 11 %		$C_7H_{15CONH_2}$ 39 %	$C_8H_{17CONH_2}$ 35 %	$C_9H_{19CONH_2}$ 38 %
$C_nH_{2n-2}O$											
$C_nH_{2n+3}NO$											
$C_nH_{2n-3}NO_2$ (glutarimide)											
$C_nH_{2n+1}NO_3$											
$C_nH_{2n+3}NO_3$											
$C_nH_{2n+4}N_2O_2$											
Miscellaneous	NH_3 , 95 %; H_2O , 294 %; $[N_2]$, 24 %; CO , 11 %; CO_2 , 11 %; $*H(C_2H_3CONH_2)_2H$, 39 %										

Classification is based on their compositional formulae, possible structure, and the relative intensities of adducts. The acrylamide oligomer is marked as *asterisk*

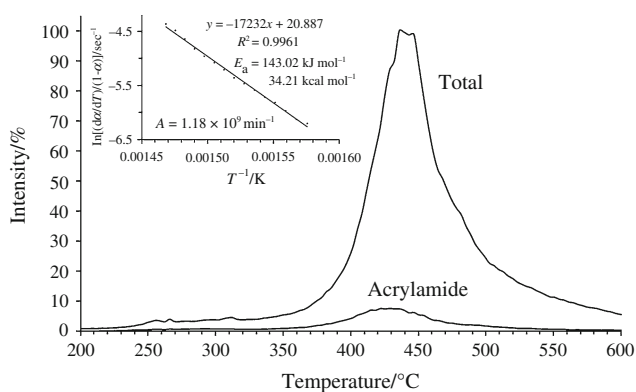


Fig. 2 Evolution profiles of thermal products during pyrolysis of PAA in nitrogen, shown by total ion and selected ion chromatograms. 1 total ion, 2 acrylamide. *Inset* Arrhenius plot for acrylamide signals over the temperature range 350–400 °C

Apparent activation energies for PAA decomposition

The apparent activation energy (E_a) of a reaction is considered to be an energetic threshold for that reaction. Thus, E_a is commonly determined to evaluate the thermal stability of polymers. We used the integral method of Knümann et al. [20] to evaluate E_a for the pyrolysis of PAA.

A pyrogram (thermogram, multi-ion detection) obtained from an EGA system gives the relative number of decomposition product molecules and indicates their production rates. The degree of conversion at any temperature T can be obtained from the area (determined by integration) under the program curve between the temperature at the start of the signal, T_0 , and T .

The ionic signal (i) acquired from real-time multiple ion detection of chemicals released from thermally decomposed specimens, such as acrylamide, has been used to obtain the functional (α) form of kinetic rate expressions. From plots of $\ln[(d\alpha/dT)/(1-\alpha)]$ vs. $1/T$, Arrhenius parameters such as E_a and the pre-exponential factor (A) can be determined. We measured the intensities of the Li^+ adduct signals at m/z 78 over the temperature range 350–400 °C in a nitrogen atmosphere to obtain the rate expressions for PAA degradation, with the assumptions that (i) a simple correlation exists between the adduct ion signal of the acrylamide product and acrylamide concentrations, and (ii) the decomposition reaction is first order (unimolecular). The slopes of the plots of temperature versus signal intensity in the region were constant (Fig. 2). We calculated an E_a of 143.02 kJ mol⁻¹ with an A of 1.18×10^9 from the plots for acrylamide.

Conclusions

Here, we describe how EGA–IAMS can provide information on the thermal decomposition products of PAA,

including acrylamide, in a controlled environment. EGA–IAMS is a simple and fast method that can be used with a small sample size, allowing rapid qualitative and semi-quantitative analysis. This method has definite advantages over conventional direct inlet probe–mass spectrometry with electron impact ionization. IAMS excludes the greater complexity of electron impact mass spectra interpretation due to the superimposition of several electron ionization fragmentation processes.

The mass chromatogram (pyrogram) of the many products associated with reaction temperature could be informative for kinetic studies to show how acrylamide, a neurotoxin, and animal carcinogen, is released. The activation energy of the thermal decomposition of acrylamide exhibited different behaviors in different environments. Under nitrogen, the activation energy of acrylamide degradation was 143.02 kJ/mol. This information will be helpful in understanding acrylamide release from PAA.

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