MASS SPECTROSCOPY OF SYNTHETIC POLYMERS

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Abstract – Pyrolysis-Mass spectroscopy can be applied to
determine the primary structure of macromolecules and to
investigate selective thermal degradation mechanisms.
The polymer samples are heated directly in the ion source
of a mass spectrometer. The high sensitivity of the instrument
allows us to follow pyrolysis mechanisms even at degradation
rates of less than 1 %/min. Low degradation rates mean low
pyrolysis temperatures at which only the activation energies
of very selective thermal degradation mechanisms are achieved.
The resulting mass spectra allow identification of the pyrolysis
products and information about the structure of polymers
and copolymers is available.

Introduction

The thermal degradation behaviour of polymers has been studied extensively
during the last 40 years (Ref. 1-3) and a first pyrolysis experiment was
reported as early as 1860, which described the preparation of isoprene
from natural rubber (Ref. 4). In these investigations the central points of
interest were the pyrolytic processes of polymers, to know their mechanisms
and degradation products under different conditions (air, inert gases,
vacuum, low and high temperatures) and to look for high temperature resistant
and inflammable plastic materials. The widely used techniques were the
preparative pyrolysis with trapping of volatile degradation products at
different temperatures, their fractionation, separation and identification
by classical or spectroscopical analytical methods (IR, GC, LC, TLC and
partially MS), as well as the analytical pyrolysis by combined pyrolysis-
gas chromatography (Py-GC) and pyrolysis-gas chromatography-mass spectro-
metry (Py-GC-MS). Those investigations which already had been reviewed in
several monographs (Ref. 1-3, 5) will not be discussed in this paper
which is devoted to the application of pyrolysis-mass spectrometry to
investigate the structure and selective thermal degradation reactions of
some synthetic high polymers.

Pyrolysis-Mass Spectrometry

In electron impact-mass spectrometry organic compounds are evaporated into
the gas phase and usually ionized by interaction with an electron beam and
abstraction of an electron from the molecule. As this ionization process is
not a real electron impact the energy transmitted to the molecule cannot be
controlled. Experiments have shown that cations (molecular ions or parent
ions) are produced, if the electron beam energy exceeds the appearance
potential of organic compounds (about 9 - 13 eV; Ref. 6). With increasing
electron voltage, additional energy can be transferred to the molecular ion,
which together with the thermal excitation from evaporation is used to
stabilize the primary radical-ions by further fragmentation reactions. The
intensity of fragment ions increases up to 40 eV more than the intensity of
the molecular ions, whereas between 40 and 100 eV a nearly constant ratio is
found. The mechanisms of electron-impact induced fragmentation reactions are
characteristic for functional groups or classes of organic compounds and can
be used to identify unknown molecular ions.
If polymers are brought into a mass spectrometer, they neither can be eva-
porated nor ionized. Upon heating the polymer samples, the temperature of
initial thermal decomposition can be detected very sensitively, since the
produced volatile pyrolysis products are ionized and registered as total ion

current before leaving the ion source. As the sensitivity of a mass spectro-
meter is in the range of 10^{-9} g, a sufficient amount of pyrolysis products
is evaporated at degradation rates of about 1 %/min (% weight loss of
polymer/min) . Low degradation rates mean low pyrolysis temperatures and
selective degradation mechanisms, which would preserve characteristic
structural elements in the pyrolysis products and correspond to the
assumption that diagnostic fragments allow the elucidation of degradation
mechanisms.
Generally synthetic polymers can be classified into four different types
of thermal degradation behaviour:

1. Statistical cleavage of the polymer chain

2. Degradation from the endgroup or an activated center via a "zip"
   mechanism (retropolymerization to one product or to the monomer)

3. Thermal degradation and/or intramolecular reactions of side chains
   in vinyl polymers as a pre-reaction of main chain cleavage

4. Thermal degradation via cyclic oligomers

Taking the less complicated type of statistical thermal degradation of
synthetic polymers the following model of pyrolysis-mass spectrometry can
be supposed (Ref. 7, 8)

$$R\{oligomers\}R^1 \xrightarrow{z+e} \begin{array}{l} \text{"molecular ions"} \\ \text{fragments} \end{array} \quad (2) \tag{1}$$

| macromolecule | volatile pyrolysis products | ions, fragments |

Low degradation rates mean that only a few of all bonds in the macromole-
cule are cleaved and that the pyrolysis should still contain the intact
structure unit one, two or several times. The subsequent "electron impact"
yields molecular ions of the pyrolysis products as well as further frag-
mented ions. The mechanisms of the electron impact induced fragmentation
depend on functional groups and are usually well known from mass spectro-
metric literature of organic compounds.
Applied to a polyester like poly(ethyleneterephthalate) the model of
equation 1 implies that thermal degradation should yield a mixture of
oligomeric esters.

$$-(CO-Ph-CO-O-CH_2-CH_2-O)- \xrightarrow{\Delta}$$
$$R-(CO-Ph-CO-O-CH_2-CH_2-O)_{1,2,3...}R' \tag{2}$$

Low molecular weight esters of terephthalic acid are known to undergo an
α-cleavage into carboxonium ions as a characteristic fragmentation reaction
(Ref. 9) followed by a partial elimination of carbon monoxide.

$$R-O-CO-Ph-C\overset{|O|^+}{\underset{}{\lessgtr}}O-R \xrightarrow{-\cdot OR} R-O-CO-Ph-C\equiv O|^+ \tag{3}$$
$$\downarrow_{-CO}$$
$$R-O-CO-Ph^+$$

Therefore, if a mixture of thermally formed terephthalic esters (Eq. 2)
is further fragmented into the ions shown in equation 3, their masses
allow the identification of the structure of the endgroup R and the
corresponding pyrolysis mechanism.
The pyrolysis-mass spectrum of poly(ethyleneterephthalate) (PET) at 350 °C
is shown in figure 1.
The molecular weight of the structural unit is 192 and the differences
of 192 mass units between the peaks at 917, 725, 533, 341 and 149
indicate that a mixture of oligomeric ions is formed which originate by
the same pyrolysis and fragmentation mechanisms.
The fragment m/e 149 is assigned as the carboxonium ion of terephthalic
acid. Since in previous studies terephthalic acid was identified as one
pyrolysis product of PET (Ref. 10, 11), it can be deduced that the series
of m/e 149 - 917 corresponds to oligomers with a thermally formed
carboxyl endgroup:

Figure 1: Pyrolysis—mass spectrum of poly(ethyleneterephthalate) at 350 °C

$$H \text{+} O-CO-Ph-CO-O-CH_2-CH_2 \text{+}_x O-CO-Ph-C\equiv O \text{|}^{\oplus}$$

m/e(x)   149(0)   341(1)   533(2)   725(3)   917(4)

The supposed pyrolysis mechanism is the thermal cis-elimination (Eq. 4) which must simultaneously yield carboxonium ions with a thermally formed vinylester endgroup (Eq. 5).

(4)

(5)

m/e 149-917

m/e(x)   175(0)   367(1)   559(2)

Scheme 1 shows that the fragment m/e 175 originates from seven or more different pyrolysis products and the fragment m/e 367 from five or more which means that the amount of detected species is decreased by frag-mentation.

A more detailed discussion of the pyrolysis—mass spectrum of PET and other aromatic polyesters has been reported elsewhere (Ref. 12).

~O-(CH₂-CH₂-O-CO-Ph-CO-O-(CH₂-CH₂-O-CO-Ph-CO-O-(CH₂-CH₂-O-CO-Ph-CO-O-(CH₂-CH₂-O-CO-Ph-CO~

CH₂=CH-O-CO-Ph-CO-OH

CH₂=CH-O-CO-Ph-CO-O-CH=CH₂

CH₂=CH-O-CO-Ph-CO-O-CH₂-CH₂-O-CO-Ph-CO-OH

CH₂=CH-O-CO-Ph-CO-O-CH₂-CH₂-O-CO-Ph-CO-O-CH=CH₂

CH₂=CH-O-CO-Ph-CO-O-CH₂-CH₂-O-CO-Ph-CO-O-CH₂-CH₂-O-CO-Ph-CO-OH

CH₂=CH-O-CO-Ph-CO-O-CH₂-CH₂-O-CO-Ph-CO-O-CH₂-CH₂-O-CO-Ph-CO-O-CH=CH₂

CH₂=CH-O-CO-Ph-CO-O-CH₂-CH₂-O-CO-Ph-CO-O-CH₂-CH₂-O-CO-Ph-CO-O-CH₂-CH₂-O-CO-Ph-CO-OH

CH₂=CH-O-CO-Ph-C≡O⊕   m/e 175

CH₂=CH-O-CO-Ph-CO-O-CH₂-CH₂-O-CO-Ph-C≡O⊕   m/e 367

CH₂=CH-O-CO-Ph-CO-O-CH₂-CH₂-O-CO-Ph-CO-O-CH₂-CH₂-O-CO-Ph-C≡O⊕   m/e 559

or   CH₂=CH-O-(CO-Ph-CO-O-CH₂-CH₂-O)ₓ-CO-Ph-C≡O⊕   m/e(x)   175(0)   367(1)   559(2)

Scheme 1: Decomposition scheme of PET into carboxonium ions with a
thermally formed vinylester endgroup

With the exception of those which retropolymerize into the monomer vinyl-
polymers generally show a more complicated degradation behaviour.
A very clear example of a three-step pyrolysis of a vinyl polymer had been
given with the poly(p-benzenesulfonamidomethacrylamid) which shows at 280,
360 and 420 °C completely different mass spectra (Fig. 2a, 2b and 2c;
Ref. 13). This polymer starts to form cyclic imid structures above 240 °C.
The pyrolysis-mass spectrum recorded at 280 °C (Fig. 2a) indicates the
elimination, evaporation and ionization of pure sulfanilamid, showing the
molecular ion (m/e 172, 100 %) and typical fragments at m/e 156, 108, 92
and 65.

Figure 2: Pyrolysis-mass spectra of poly(p-benzenesulfonamidomethacrylamid)
          at 280 °C (a), 360 °C (b) and 420 °C (c) and 15 eV

At 360 °C the high intensities of peaks at m/e 93 (aniline), m/e 64 (SO_2)
and m/e 17 (NH_3) show that the remaining side chains are cleaved off.
Further fragments of higher masses at 420 °C (Fig. 2c, m/e 189, 201, 215
and 229) account for the formation of glutaric imid derivatives (Fig. 3).
A clear differentiation of these thermal degradation reactions allows a
thermal mass fragmentogram, which was obtained by pyrolyzing the polymer
with a temperature program, recording in 20 °C intervals a mass spectrum on
the connected data system and plotting the intensities of characteristic
ions of all mass spectra versus temperature (Fig. 4).

The thermal degradation behaviour of polystyrene (PS) has been investigated
extensivly and even Staudinger described in 1929 the pyrolysis of this
polymer (Ref. 14). Polystyrene yields under pyrolysis conditions mainly the
monomer and it was therefore proposed that PS degrades by radical depoly-
merization essentially by unzipping to the monomer. Small amounts of dimer,
trimer and tetramer show that the initially formed radicals are partially
stabilized by disproportionation.
Additionally, it had been observed that the molecular weight of PS decreases

Figure 3: Thermal degradation pathways of poly(p-benzenesulfonamidometh-
acrylamid) at different temperatures

Figure 4: Mass fragmentogram of poly(p-benzenesulfonamidomethacrylamid),
heating rate 50 °C/min and 15 eV

rapidly in the initial stage of thermal degradation and some authors have
explained this behaviour by suggesting "weak links" to various degrees in
the polymer (Ref. 15-17). It was then proposed that some head-to-head
linkages exist in the radically initiated styrene polymer which might
decrease the thermal stability.
Figure 5 compares the pyrolysis-mass spectra of head-to-tail (HT) and a
pure head-to-head polystyrene (HH) which has been obtained by polymeriza-
tion of 2,3-diphenyl-1,3-butadiene and a selective hydrogenation of the
double bond in the polymer chain (Ref. 18).

Figure 5: Pyrolysis-mass spectra of HT (above) and HH polystyrene (below)
          at 320 °C

The intensities of styrene (m/e 104) and the linear dimers (m/e 208) and
trimers (m/e 312) of styrene in the thermal degradation spectrum of HT PS
related to the sum of all detected ions are 57.3 %Σ, 3.7 %Σ and 2 %Σ
which, however, can only approximate the ratio of thermally formed monomer,
dimer and trimer.
The pyrolysis-mass spectrum of the HH polystyrene shows peaks for the
monomers to pentamers of styrene. Their relative sum intensities are 4.0 %Σ
(monomer), 3.7 %Σ (dimer), 1.1 %Σ (trimer), 0.5 %Σ tetramer) and 0.2 %Σ
(pentamer, m/e 520); their abundance and relative ratio is significantly
changed in comparison to the degradation products of HT PS. This implies
that a probable thermal degradation of HH PS by unzipping to the monomer
can be neglected and that head-to-head linkages even increase the
thermal stability.
An important characteristic of HH PS is its ability to form stilbene
(m/e 180) by thermal degradation (Ref. 19).

The application of pyrolysis-mass spectrometry to the structure elucidation
of copolymers - e.g. investigation of sequences (Ref. 20, 21) and deter-
mination of compositions (Ref. 22-24) - has been described. It could be
demonstrated that the alternating structure of some copolyamides, which
had been characterized independently, can also be established by mass
spectrometry (Ref. 20). Figure 6 compares the mass spectra of the alter-
nating copolyamides of p-aminobenzoic acid and γ-aminobutyric acid (c)
and the corresponding homopolyamides (a, b).
Without explaining all spectra in detail, the proof of pyrolysis products
containing more than one structure (monomer) unit can be used to detect
alternating sequences. The weight of the structure unit of poly(imino-
carbonyl-1,4-phenylene) is 120, which means that fragments of higher
masses than m/e 137 (NH_3-Ph-CO-NH_2 +) in figure 6a indicate two neigh-
bouring aromatic units, as well as higher masses than m/e 72 (NH_2-CH_2-CH_2-
-C≡O| +) in figure 6b two aliphatic units. The pyrolysis-mass spectrum
of the alternating copolyamid (Fig. 6c) demonstrates that no pyrolysis
product or fragment is formed containing neighbouring aromatic or aliphatic
structure units.

Figure 6: Pyrolysis-mass spectra of poly(iminocarbonyl-1,4-phenylene) (a),
         poly(iminocarbonyltrimethylene) (b) and the alternating
         copolyamid (c) at 300 °C

Figure 7: Mass fragmentogram of the alternating copolyamid of p-amino-
         benzoic and γ-aminobutytic acid

Earlier preparative experiments with this copolyamid have shown that at
elevated temperatures monomeric butyrolactam is eliminated, whereas the
IR and NMR spectra of the residue become more and more similar to those of
the aromatic homopolyamid. The technique of mass fragmentography (Fig. 7)
allows us to follow this degradation reaction directly. Above 280 ^{o}C an
intensive formation of butyrolactam is observed which reaches a maximum above
420 ^{o}C. Parallel fragments of alternating sequence can be detected which
also disappear at 410 ^{o}C. Above 380 ^{o}C fragments arise containing two aro-
matic structure units ($NH_2-Ph-CO-NH-Ph-C=O$ $^+$, $NH_2-Ph-CO-NH-Ph$ $^+$) and
indicate pure aromatic sequences in the polymeric residue.

A possible correlation between the intensities of monomer specific frag-
ments and the composition of the copolymer by pyrolysis-FI-mass spectro-
metry had first been reported by Hummel and Düssel (Ref. 25). Recent
investigations in this field have demonstrated that this technique might
become a fast and exact determination method of copolymer compositions
(Ref. 22-24).
To elucidate the composition of a copolymer system a calibration curve is
required, obtained from copolymers of known compositions and the correspon-
ding homopolymers. The relative sum intensities of two or more monomer
specific fragments are plotted versus the known compositions. If repetitive
measurements of this known copolymers are carried out an arithmetic
average value and a standard deviation can be calculated, which allows us to
assign the exactness of the method. This procedure had recently been
illustrated by copolyesters of glycolic and lactic acid (Ref. 24) which
form the monomer specific fragments m/e 42 ($CH_2=C=O$ $^+$) and m/e 116 (glyco-
lide) and m/e 56 ($CH_3-CH=C=O$ $^+$).
Table 1 shows the intensities of these fragments from five separate measure-
ments, obtained from copolyesters with 0 , 3.5 ,11.7 , 36.0 , 47.0 , 59.0 ,
78.0 and 100 mol-% of incorporated lactic acid.
The calculated standard deviation of e.g. 1.52 at an arithmetric average
value of 56.7 mol-% (fragment m/e 42, first line of table 1) means that
the exact value of each measurement must be found with a probability of
68.3 % in the range of 56.7 ± 1.52 mol-%.
Figure 8 shows the calibration curve obtained from table 1 which had been
reexamined by copolyesters of unkhown compositions. Independent determina-
tions by NMR spectroscopy confirmed an error limit of ± 1.5 mol-%.

Figure 8: Plot of the relative sum intensities of the fragments m/e 42, 56
          and 116 versus the content of incorporated lactic acid
          (calibration curve)

Table 1: Calculation of the arithmetic average value and standard
deviation s of the relative sum intensities of the
fragments m/e 42, 56 and 116 from 5 different measure-
ments of copolyesters of lactic and glycolic acid

mol-% incorporated lactic acid	measurement[x]					arith. average	s[xx]
	1.	2.	3.	4.	5.		
m/e 42							
0	57.8	55.6	54.9	58.6	56.6	56.7	1.52
3.5	56.9	53.7	52.1	55.4	57.9	55.2	1.77
11.7	52.0	53.1	52.9	54.6	52.9	53.1	0.94
36.0	49.2	46.8	47.0	44.3	45.2	46.5	1.88
47.0	28.9	32.5	30.3	31.9	29.0	30.5	1.67
59.0	24.4	27.3	25.2	28.0	28.1	26.6	1.70
78.0	13.3	13.8	14.1	13.6	12.7	13.5	0.53
100	2.1	3.7	2.7	2.0	1.9	2.5	0.79
m/e 56							
0	-	-	-	-	-	-	-
3.5	1.8	1.8	1.7	1.5	1.7	1.7	0.12
11.7	2.3	2.9	2.9	2.4	3.0	2.7	0.32
36.0	7.8	8.4	8.6	8.2	7.5	8.1	0.45
47.0	10.5	10.1	11.6	10.2	10.6	10.6	0.60
59.0	14.7	14.0	14.3	12.8	13.2	13.8	0.78
78.0	18.9	20.6	20.3	20.7	19.0	20.1	0.91
100	42.2	41.2	44.0	39.5	42.1	41.8	1.67
m/e 116							
0	14.6	15.6	14.8	13.2	14.3	14.5	0.87
3.5	13.0	12.9	14.1	13.8	13.2	13.4	0.52
11.7	11.9	13.3	12.9	10.8	11.1	12.0	1.09
36.0	8.4	7.0	7.9	8.6	8.6	8.1	0.68
47.0	5.4	5.4	4.7	4.6	4.9	5.0	0.38
59.0	3.9	3.5	3.1	3.3	3.7	3.5	0.32
78.0	1.7	1.9	1.6	1.7	2.1	1.8	0.20
100	-	-	-	-	-	-	-

[x] relative intensities in %, related to the sum of intensities of all
     fragments
[xx] approximation of s

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