MASS SPECTROSCOPY OF SYNTHETIC POLYMERS

Ingo Lüderwald

Institute of Organic Chemistry, University of Mainz, Johann-Joachim-Becher-Weg 18-20, D-6500 Mainz

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 spectrometry (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 put into a mass spectrometer, they neither can be evaporated 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 spectrometer is in the range of $10^{-5}$ 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)

\[
\text{R(oligomers)} \rightarrow \text{R}^+ 
\]

(1)

macromolecule \rightarrow \text{volatile pyrolysis products ions, fragments}

Low degradation rates mean that only a few of all bonds in the macromolecule 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 fragmented ions. The mechanisms of the electron impact induced fragmentation depend on functional groups and are usually well known from mass spectrometric 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.

\[
\text{(CO--Ph--CO--O--CH}_2\text{--CH}_2\text{--O)} \rightarrow \text{R(CO--Ph--CO--O--CH}_2\text{--CH}_2\text{--O) el, R'}
\]

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

\[
\text{R}--\text{O}--\text{CO--Ph} \rightarrow \text{R}--\text{O}--\text{CO--Ph}^+ \text{+ CO}
\]

(3)

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(ethyleneteraphthalate) at 350 °C

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).

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 fragmentation.

A more detailed discussion of the pyrolysis—mass spectrum of PET and other aromatic polyesters has been reported elsewhere (Ref. 12).
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 (SO₂) and m/e 17 (NH₃) 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 extensively 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 depolymerization 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-benzenesulfonamidomethylacrylamid) at different temperatures

Figure 4: Mass fragmentogram of poly(p-benzenesulfonamidomethylacrylamid), 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 polymerization of 2,3-diphenyl-1,3-butadiene and a selective hydrogenation of the double bond in the polymer chain (Ref. 18).

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 %, 3.7 % and 2 % 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 % (monomer), 3.7 % (dimer), 1.1 % (trimer), 0.5 % (tetramer) and 0.2 % (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 determination of compositions (Ref. 22—24) — has been described. It could be demonstrated that the alternating structure of some copolymides, which had been characterized independently, can also be established by mass spectrometry (Ref. 20). Figure 6 compares the mass spectra of the alternating copolymides of p-aminobenzoic acid and p-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—Ph—CO—NH2 +) in figure 6a indicate two neighbouring aromatic units, as well as higher masses than m/e 72 (NH—CH2—CH2—COt +) in figure 6b two aliphatic units. The pyrolysis—mass spectrum of the alternating copolyamide (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 ε-aminobutyric 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 °C an intensive formation of butyrolactam is observed which reaches a maximum above 420 °C. Parallel fragments of alternating sequence can be detected which also disappear at 410 °C. Above 360 °C fragments arise containing two aromatic structure units (NH—Ph—CO—NH—Ph—C=O +, NH—Ph—CO—NH—Ph +) and indicate pure aromatic sequences in the polymeric residue.

A possible correlation between the intensities of monomer specific fragments and the composition of the copolymer by pyrolysis—FI—mass spectrometry had first been reported by Hummel and Düessel (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 corresponding 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 (CH₂=C=O+) and m/e 116 (glycolide) and m/e 56 (CH₃—CH=C=O).

Table I shows the intensities of these fragments from five separate measurements, obtained from copolymers 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 arithmetic average value of 56.7 mol-% (fragment m/e 42, first line of table I) 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 I which had been reexamined by copolyesters of unknown compositions. Independent determinations by NMR spectroscopy confirmed an error limit of ± 1.5 mol-%.
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 measurements of copolysters of lactic and glycolic acid

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\(^{\text{K}}\) relative intensities in %, related to the sum of intensities of all fragments

\(^{\text{XX}}\) approximation of s
References

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