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Thermal degradation of different fire retardant polyurethane foams

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Abstract

The thermal behaviour of four different flame retarded polyurethane foams has been investigated. For this reason simultaneous thermal analysis/mass spectrometry (TA/MS) as well as incineration experiments on laboratory scale were carried out. Additionally the evolved gases during TA/MS measurement were adsorbed on XAD-resin and identified by means of GC-MS analysis. The results were compared to those of the incineration experiments and the degradation pathways of the flame retardants are discussed.

Keywords: Polymer; Flame retardant; Thermal analysis/mass spectrometry; Burning; Thermal degradation

1. Introduction

The increasing production output of modern society is followed by an increasing impact of waste into the ecosphere. Due to decreasing disposal site capacity, the importance of waste incineration is still increasing, especially in the disposal of polymeric materials. Due to its economic unprofitable material re- or down-cycling, often an "energy recycling" by incineration can be considered.

Since incineration as well as fire accidents may lead to toxic or harmful substances, knowledge about the thermal degradation of these substances, toxicological and ecotoxicological risk assessment of the degradation products as well as knowledge about the thermal degradation mechanism of the polymers are of interest. A useful tool for studying the degradation mechanisms is simultaneous thermal analysis/mass spectrometry (TA/MS) which has been used in several cases [1–12].

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2. Experimental

2.1. Combustion

For studies of thermal degradation of the samples we used two different degradation devices. The samples (ca. 20 mg) were investigated in a simultaneous TA/MS device consisting of a STA 429 simultaneous thermal analyser (Netzsch Gerätebau GmbH) and an on-line coupled QMG 420 quadrupole mass spectrometer (Balzers Hochvakuum GmbH). The samples were heated from ambient temperature up to 800°C using a heating rate of 10 K min^{-1} in an argon atmosphere and synthetic air. Additionally, all samples were investigated in a modified Bayer/ICI/Shell (BIS) combustion device. For this investigation, samples between 60 and 65 mg were used. The BIS combustion device is described in detail in Ref. [13].

For the enrichment and adsorption of thermal degradation products of polymers, Amberlite XAD-4® resin has been shown to be very useful [11]. For the desorption of the materials, we used acetone according to Ref. [12]. The identification of the degradation products was done by GC/MSD.

2.2. GC/MS analysis

The degradation products, formed during the dynamic heating in the STA/MS apparatus, were transferred by a gas stream to an adsorption device and analysed by GC/MSD after desorption with acetone. The identification of the products was performed by means of their mass spectral data and comparison of the retention times with reference materials. The GC/MSD combination consisted of a HP 5890 gas chromatograph and a HP 5970 mass selective detector. The conditions for the analysis were as follows: retention gap, 2.5 m phenyl-silicone, 0.35 mm i.d.; column, SE-54, 50 m, 0.35 mm i.d., 0.25 μm film; carrier gas, helium; 105 kPa; injector, split/splitless injector; 280°C; mode, spitless, 0.9 min splitless time; transfer line, 280°C; temperature programme, 27°C, 1 min isothermal, 60°C, 20 K min^{-1}, 1 min isothermal, 150°C, 3 K min^{-1}, 280°C, 5 K min^{-1}, solvent delay, 3 min; detector, HP MSD 5970 (70 eV); modus, SCAN.

2.2. Sample materials

We investigated four different flame retarded polyurethane foam samples. The samples were self-prepared on laboratory scale and contained 10–11 weight % different flame retardants. The structures of the flame retardants (organic phosphoric esters); tris(β-chlorethyl)-phosphate (TCEP), tris(β-chlor-isopropyl)-phosphate (TCPP), (tris-(β,β'-dichlorisopropyl)-phosphate (TDCP) and diethyl-*N*,*N*-bis-(2-hydroxyethyl)-aminomethylphosphonate (DAMP) are given in Fig. 1.

3. Results and discussion

During thermal analysis, all samples show quite similar behaviour. Example TA

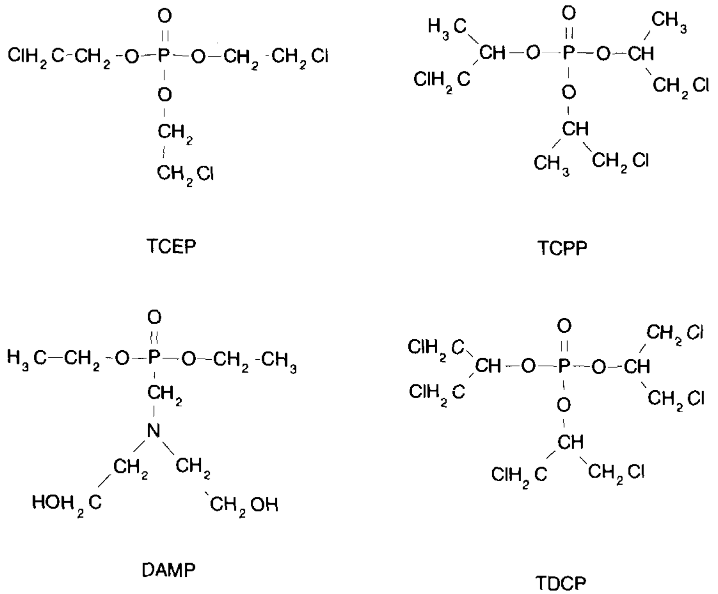

Fig. 1. Structure of the flame retardants investigated.

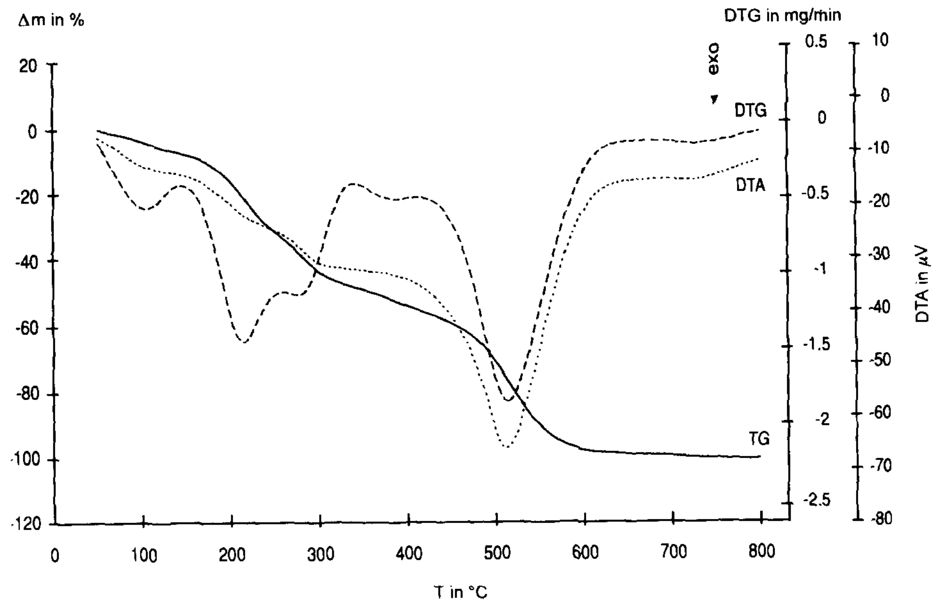

Fig. 2. TA curves of PUR-TCPP (air atmosphere).

Table 1
TA data

Sample	DTG maximum/°C	DTA maximum/°C	Δm/%
PUR-TCPP	99	–	7
	215	–	25
	280	–	13
	391	–	7
	512	512	45
			$\Delta m_{tot} = 97$
PUR-TCEP	113	–	8
	232	–	32
	334	–	21
	503	505	23
	753		16
			$\Delta m_{tot} = 100$
PUR-TDCP	101	–	7
	240	–	36
	506	507	53
	736	–	3
			$\Delta m_{tot} = 99$
PUR-DAMP	263	–	37
	339	–	15
	505	509	38
	741	738	10
			$\Delta m_{tot} = 100$

curves from the investigation of PUR containing TCPP as flame retardant in air atmosphere are shown in Fig. 2.

The degradation of the samples occurred in the selected temperature range (20–800°C) in several steps accompanied by quite unspecific DTA curves. Except one exothermic effect at about 500°C (in the case of PUR-DAMP additional 738°C) no further peaks can be obtained. The DTG curves show several peaks in accordance with multistep TG curves. The data of the TA investigations are summarized in Table 1.

Several investigations on thermal degradation of PU foam found in the literature were carried out by means of pyrolysis/mass spectrometry [13–16]. During these experiments, many decomposition products could be identified. Beneath the reformation of the polyol- and isocyanate compounds, their hydrolysis products (amines) have been detected.

Other pyrolysis studies were carried out to determine different PU isocyanate compounds [17] or differentiate between polyester- and polyether-based resins [18]. Others have determined the emission of HCN, CO and CO_2 [19]. Grassie et al. have also studied the thermal degradation of PU resins by means of thermal analysis [20] and discussed the role of phosphorus compounds as flame retardants [21].

In our experiments, during on-line mass spectrometry, intensive signals at *m/z* 101, 87, 73 and 58 can be detected at about 250–300°C within all samples. These fragments show the degradation of the polyole component. Since these fragments can be associated with different general formulas and different isomers, a distinction between polyester- and polyether based PU could not be done.

Within the second degradation step at about 400°C, intensive signals at *m/z* 93 and 107 can be obtained. These ions can be associated with aniline and methylaniline, which were formed during the degradation of 4,4′-methylendiphenyldiisocyanate (MDI). In this step of degradation, a reformation of the isocyanate compounds can be obtained. The pathway of the degradation of MDI is given in Fig. 3.

In the range of 200–220°C, the mass spectra of all samples are different. Since the samples are just different by the flame retardant, it can be assumed that in this range the degradation of the additive will take place and the fragments found in the mass spectrometer belong to their degradation products. Therefore, the different samples are discussed separately in the following.

3.1. PUR-TCPP

From the sample with TCPP as flame retardant added, intensive signals at *m/z* 63, 65, 76, 99, 125, 139 and 157 can be registered (see Fig. 4). The fragments at *m/z* 99, 125, 139 and 157 belong to phosphorus containing compounds and the strong signals at *m/z* 63 and 65 belong to the $CH_2Cl–CH_2^+$ ion. A possible degradation pathway of the flame retardant is given in Fig. 5.

The analysis of the on-line sampled degradation compounds (adsorption on XAD-4 resin) by means of GC-MSD also leads to this result. Beneath some nitrogen containing compounds such as aniline, methylaniline, benzonitrile, phenylsiocyanate a great number of diol components could be identified. Furthermore, degradation products of the flame retardant could be identified. Organic phosphoresters (cf. Fig. 6, peak 21) as well as some chlorinated hydrocarbons like 1,3-dichlorpropane and 2-chloro-2-proanole could be detected. In Table 2 the identified compounds corresponding to the peak numbers are summarized.

For comparison of these experiments with standard furnace incineration experiments, additional investigations were carried out in the BIS apparatus. The samples were burned at 400 and 600°C and the evolved degradation products adsorbed and also investigated by GC-MSD. As can be seen from the total ion chromatograms shown in Figs. 7 and 8, this leads to similar results. Part of the aniline and methylaniline did react with the solvent (acetone). Therefore, further experiments were carried out using isopropanol as solvent.

3.2. PUR-TDCP

The sample with TDCP added shows strong signals at *m/z* 75, 77, 79, 81, 110, 112 and 114 (cf. Fig. 9) in the range of 200–220°C. These fragments belong to the 1,3-

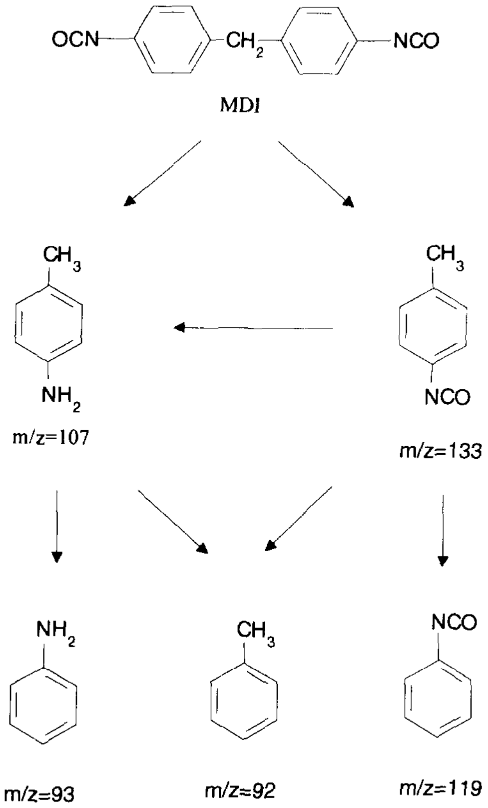

Fig. 3. Formation of amines, isocyanates and toluene from MDI.

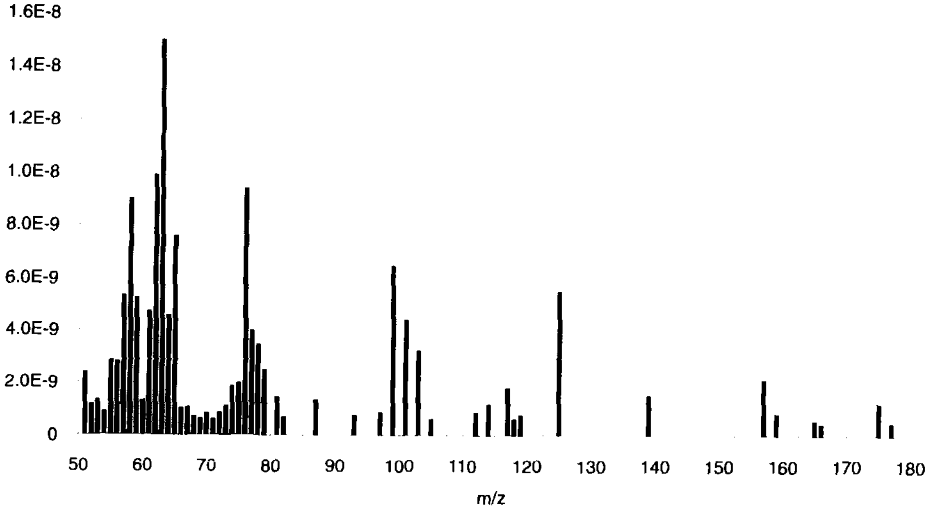

Fig. 4. Mass spectrum of PUR-TCPP in air atmosphere $T = 210°C$.

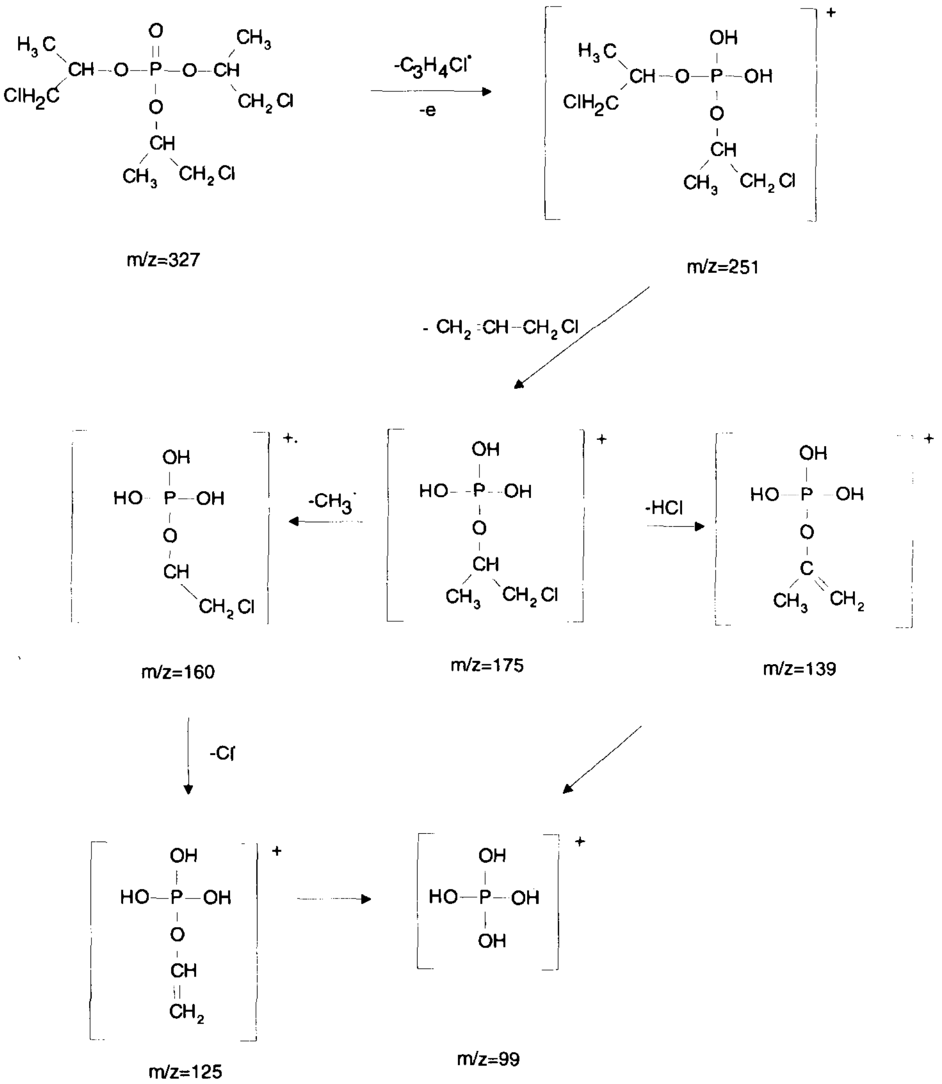

Fig. 5. Possible degradation pathways of TCPP.

dichlorpropane which was formed during the degradation of the flame retardant. The formation of 1,3-dichlorpropane could be confirmed by the BIS experiment and GC-MS analysis of the adsorbed volatiles from the TA/MS experiment. The degradation pathway of TDCP and building of dichlorpropane is shown in Fig. 10.

3.3. PUR-TCEP

Assuming a similar degradation of TCEP, the cleavage of vinyl-chloride should be

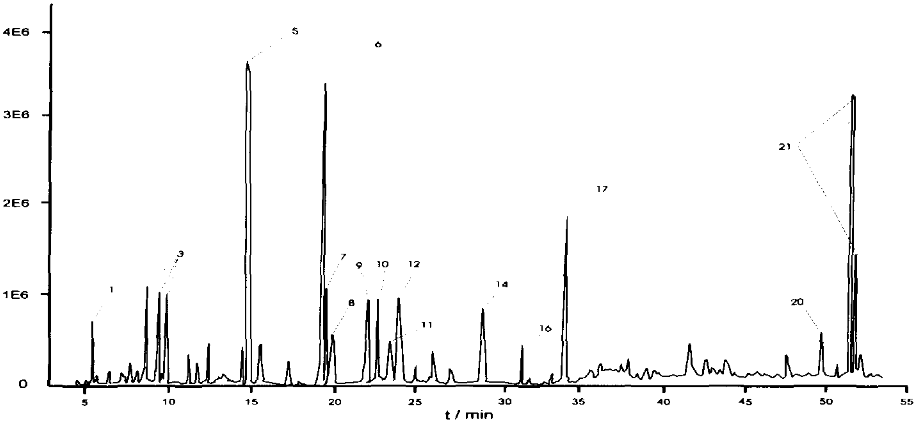

Fig. 6. Chromatogram of XAD-4-extracts from PUR-TCPP (TA/MS-experiment).

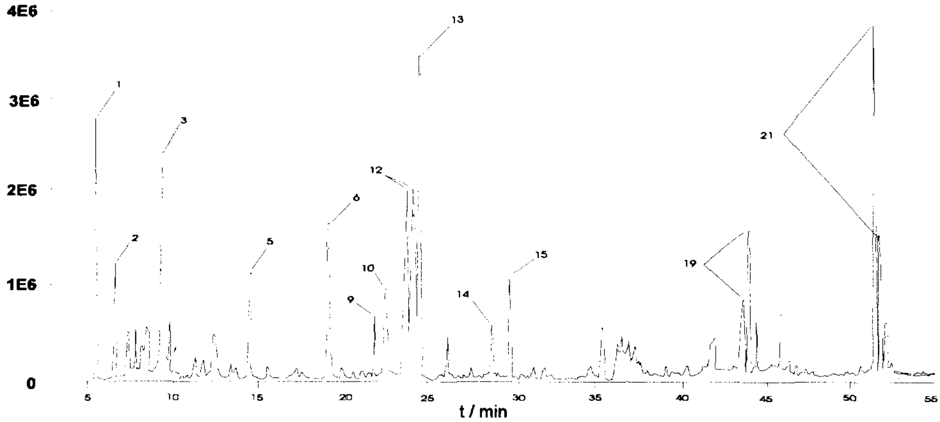

Fig. 7. Chromatogram of XAD-4 extracts from PUR-TCPP ($T = 400°C$, BIS experiment).

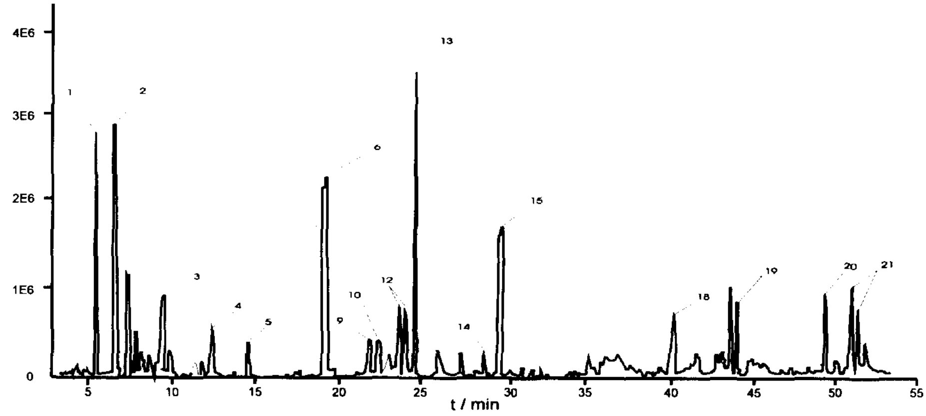

Fig. 8. Chromatogram of XAD-4-extracts from PUR-TCPP ($T = 600°C$, BIS experiment).

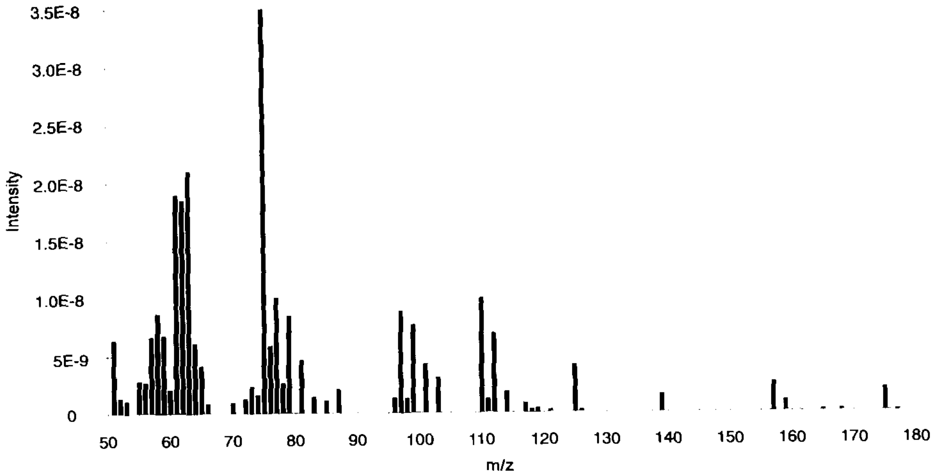

Fig. 9. Mass spectrum of PU-TDCP ($T = 210°C$, TA/MS experiment).

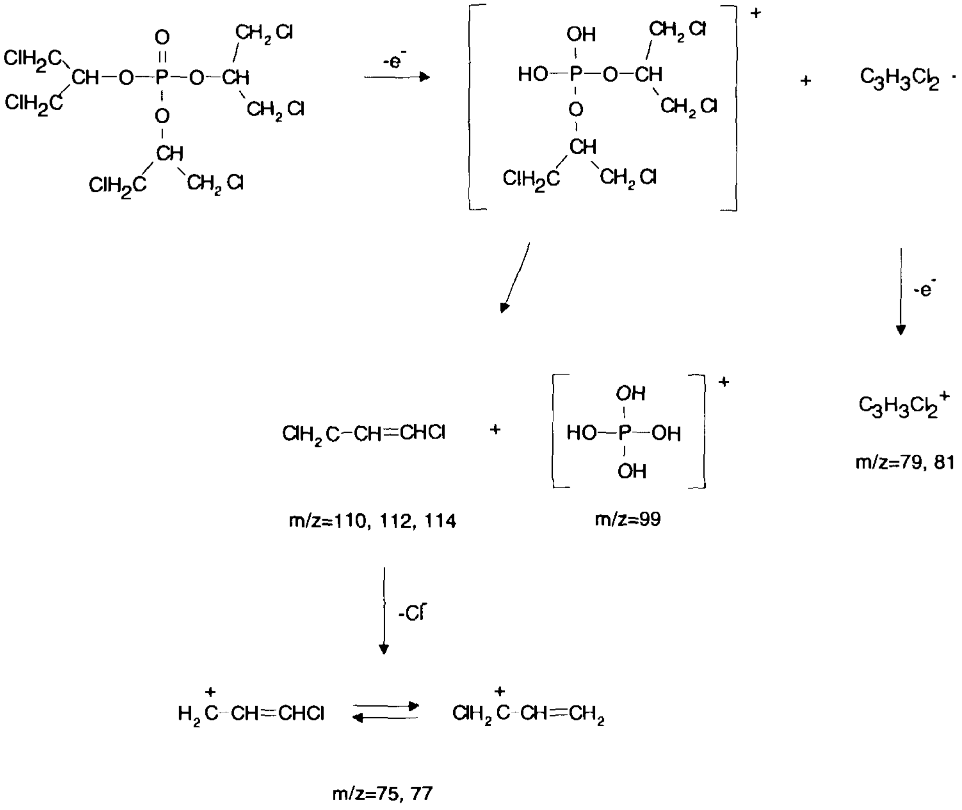

Fig. 10. Degradation pathway of TDCP.

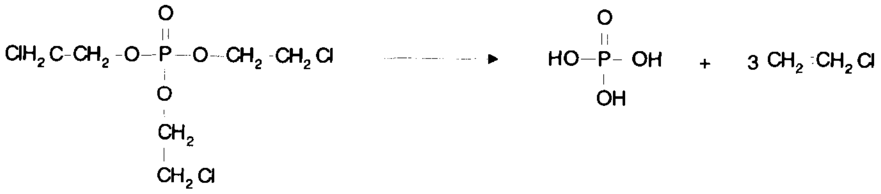

Fig. 11. Formation of vinyl chloride from TCEP.

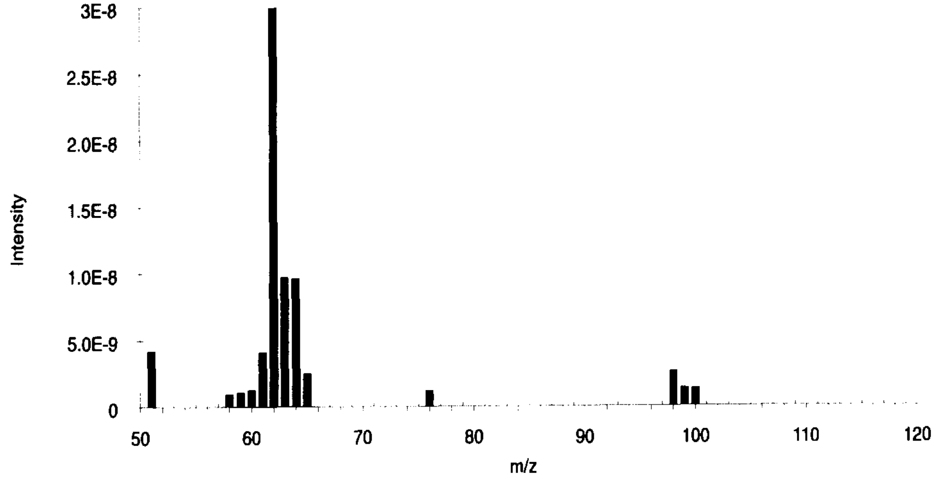

Fig. 12. Mass spectrum of PU-TCEP (T = 210°C, TA/MS experiment).

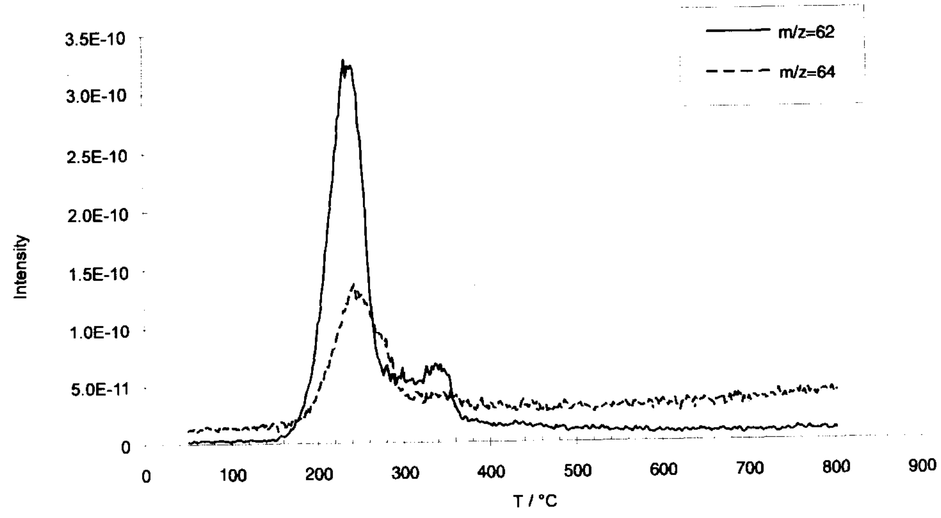

Fig. 13. Ion current intensity of m/z 62 and 64 from PUR-TCEP.

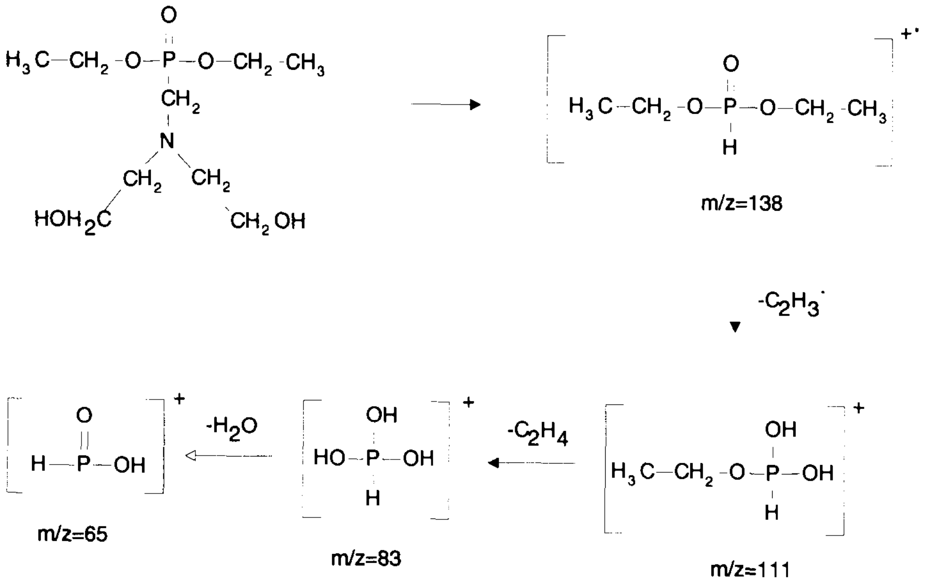

Fig. 14. Degradation pathway of DAMP.

obtained (cf. Fig. 11). As can be seen from the mass spectrum at 210°C in Fig. 12, strong signals at *m/z* 62 and 64 in the ratio of 3:1 can be obtained and the analysis of the volatiles by GC-MS leads to vinyl chloride. The cleaving of vinyl chloride occurs first at about 160°C and reaches its maximum at 220°C. A second, but less intensive maximum can be obtained at about 340°C (cf. Fig. 13).

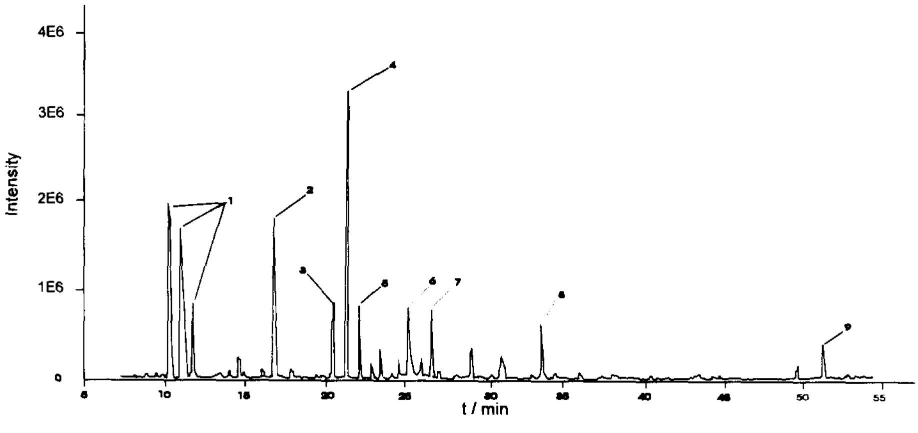

Fig. 15. Chromatogram of XAD-4 extracts (PUR-DAMP, TA/MS-experiment).

Table 3
Identified compounds from the degradation of PUR-DAMP

Peak no.	Substance
1	Diol compounds
2	2-Methoxyethanole
3	Diethylphosphinate
4	Aniline
5	Phenylisocyanate
6	Diol components
7	Methylaniline
8	Propylaniline
9	Phenyl urea

3.4. PUR-DAMP

The sample with DAMP added also showed a significant mass spectrum in this temperature range. The intense signals at *m/z* 111, 83 and 65 belong to phosphoric acid diethyl ether, a degradation product of DAMP (cf. Fig. 14). This is supported from the total ion chromatogram observed from the adsorbed volatiles of the TA/MS experiment (cf. Fig. 15). The identified products corresponding to the peak numbers are listed in Table 3.

4. Conclusions

The investigations have shown that on-line coupled TA/MA is a useful tool for the determination of PU degradation products. From the different mass spectrometric data in the lower temperature region (200–220°C) a distinction between different flame retarded samples could be done, and in the case of defined additives, their degradation pathway can be obtained. From the mass spectra taken at higher degradation temperatures, the decomposition of the basic resin and the reformation of the diole- and isocyanate compound could be observed. Nevertheless, due to the direct inlet mode of the mass spectrometer, no separation of the sample gases will take place. Therefore, a direct identification of the degradation products by means of TA/MS cannot be done. An additional adsorption of the sample gases and GC-MS analysis of these adsorbed compounds lead to the desired results.

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