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Effect of branching on the degradation behaviour and caloric properties of PVC[1]

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Abstract

Nine different PVC samples with defined chlorine content and degree of branching have been investigated. The aim of the work was the influence of these parameters on some caloric properties as well as the degradation behaviour and the degradation products. As expected, the heat of combustion decreases with increasing chlorine content. As determined by simultaneous thermal analysis/mass spectrometry, the volatile degradation products of the pyrolysis in nitrogen atmosphere vary. The higher the chlorine content, the higher the amount of chlorinated degradation products and the lower the amount of polycyclic aromatic hydrocarbons (PAH). A higher number of branching promotes the formation of alcylated aromatic hydrocarbons. © 1998 Elsevier Science B.V.

Keywords: Degradation; Mass Spectrometry; PVC; Thermal Analysis

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1. Introduction

Polyvinylchloride (PVC) is a widely used polymer with a high versatility of service. The amount of PVC produced in Germany was, in 1995, ca. 1.4×10^6 ton per year. Nevertheless, the use of PVC is restricted in Germany. Within the scope of the 'Chlorine discussion' in Germany, the use of PVC is called in question. Due to its high chlorine content (≈56 wt%) it is assumed, that hazardous or toxic substances will be evolved in cases of fire or during incineration. Nevertheless, within the building-trade, the amount of PVC use is still increasing.

For some special applications the temperature stability of PVC is not sufficient. For this purpose, post-chlorinated materials with chlorine contents up to 68 wt% are available.

The aim of this work was the investigation of the thermal-degradation products depending on the different branching of the PVC materials.

For this purpose, different branched PVC types of different chlorine contents were selected.

2. Materials

Three different branched PVC samples with identical chlorine contents have been photochemically post chlorinated in laboratory scale earlier [1].

The starting material as well as samples with medium and higher chlorine contents, as listed in Table 1, have been investigated.

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Table 1
Sample materials; characteristic data

Sample	Chlorine content/ mass%	Side-chains per 100 000 g/mol	T_g/°C	Δc_p/(J/gK)
1. PVC-Sample (standard)				
1.1	56.9	1	84.3	0.30
1.2	56.6	3	86.3	0.28
1.3	56.6	11	83.7	0.29
2. Medium chlorine content				
2.1	61.6		88.5	0.18
2.2	60.8		91.5	0.15
2.3	61.3		85.8	0.14
3. High chlorine content				
3.1	66.6		n.d.	n.d.
3.2	66.9		102.4	n.d.
3.3	65.3		85.9	0.07 [a]

[a] Partial glass transition, probably resulting from standard PVC content.

The effect of the chlorine content on the glass transition (temperature, specific heat capacity) as well as first degradation studies have been described elsewhere [1].

3. Experimental

3.1. Calorimetry:

The calorimetric studies were carried out on an IKA C 5000 calorimeter (IKA Analysentechnik GmbH) in the adiabatic mode.

3.2. Thermogravimetry

The simultaneous thermal analysis/mass spectrometric studies were carried out on an NETZSCH/Balzers STA 429/QMG 420 device. The operation modes were:

- simultaneous thermal analysis STA 429 (NETZSCH Gerätebau GmbH)
- weighted sample: 25 mg
- heating rate: 10 K/min
- gas flow: 100 ml/min, nitrogen

3.3. Analysis of the degradation products

The degradation products were identified in two ways. Firstly by the on-line mass-spectrometric coupling and, secondly, by an on-line adsorption, off-line GC-MS analysis of the volatiles. The operation modes were:

- simultaneous mass spectrometry (on-line): QMG 420 (Balzers AG);
- scan mode, m/z 10–210;
- scan at every 20 K;
- GC/MS-analysis (off-line);
- adsorption of the volatiles on XAD 4-resin;
- desorption using Acteon;
- gas chromatography HP 5890;
- (analytical column 94% methylsilicone, 5% phenylsilicone, 1% vinylsilicone); and
- MS Engine HP 5989 A.

4. Results

4.1. Calorimetry

The calorimetric results form the investigation of some of the samples are listed in Table 2, the sample numbers are the same as shown in Table 1.

Table 2
Calorimetric values

Sample No.	Heat of combustion [a]/(kJ/g)
1.1	20.9
1.3	20.8
3.1	17.4
3.2	17.5

[a] Error: ±0.12%.

4.2. Thermal analysis/mass spectrometry

The degradation of PVC results in two steps up to a maximum of 600°C. With an increasing chlorine content, the total weight loss is decreasing from ca. 90% down to 74% for the sample with a chlorine content of ca. 66%. The varying results from the different samples are summarised in Table 3, and two exemplary TA-curves are shown in Fig. 1 and 2.

The first degradation step is known as the 'dehydrochlorination'. The mean volatile degradation products are:

- hydrochloride (HCl);
- aromatic hydrocarbons (mainly benzene);
- polycyclic aromatic hydrocarbons (e.g. naphthalene $C_{10}H_8$); and
- chlorinated hydrocarbons (benzenechloride).

The second degradation step, the degradation of the remaining polymer matrix, is accompanied by the evolution of:

- alkylated aromatc hydrocarbons (e.g. toluene, xylene, ethylbenzene, ethyl-2-methylbenzene);
- chlorinated aromatic hydrocarbons (benzenedichloride, benzenetrichloride (high chlorine content));
- polycyclic aromatic hydrocarbons (1-H-indene C_9H_8, phenanthrene $C_{14}H_{10}$, fluoranthene $C_{16}H_{10}$); and
- chlorinated polycyclic aromatic hydrocarbons (naphthalenechloride $C_{10}H_7Cl$).

The 3-D scan overview, in the 50–200 mass range in Fig. 3 and 4, shows the evolution of the volatile products from the standard PVC and the CPVC with ca. 66% chlorine content.

The temperature-dependent evolution of some selected degradation products is shown in Fig. 5–10.

The following trends can be observed:

- With a higher chlorine content the amount of chlorinated hydrocarbons as degrtadations products increases. From the standard PVC only benzenechloride can be detected, while the sample with a higher chlorine content leads up to benzenetrichloride
- With increasing chlorine content the amount of polycyclic aromatic hydrocarbons (PAH) decreases.
- The number of branchings within the PVC only shows an influence on the amount of alkylated aromatic hydrocarbons. Its amount increases with the number of branchings

Further investigations will point, on the one hand, towards degradation in synthetic air and, on the other, to the non-volatile degradation products.

Table 3
Results of thermal analysis

Sample No.	Weight loss/ %			$DTG_{peak\ max}$/°C	
	1st step	2nd step	Total	1st step	2nd step
1.1	63.1	26.7	89.8	269	459
1.2	65.5	27.4	92.9	272	458
1.3	63.7	27.7	91.4	269	460
2.1	65.5	17.6	83.1	273	435
2.2	66.0	16.6	82.6	271	436
2.3	66.2	16.7	82.9	273	437
3.1	66.0	8.4	74.4	288	no peak
3.2	65.1	8.9	73.0	288	no peak
3.3	64.2	11.3	75.5	284	440

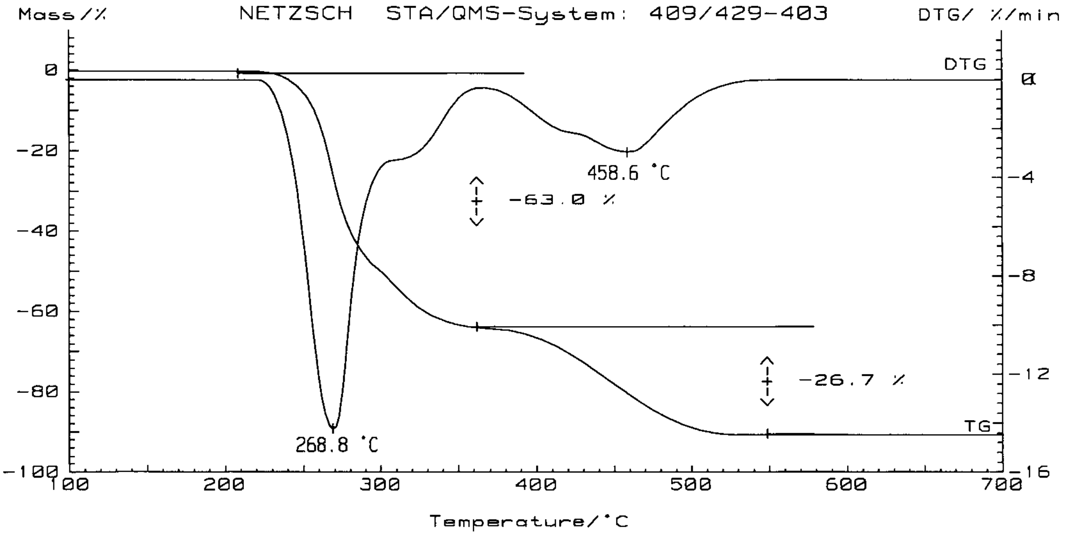

Fig. 1. TG- and DTG-curves of PVC (57% chlorine content).

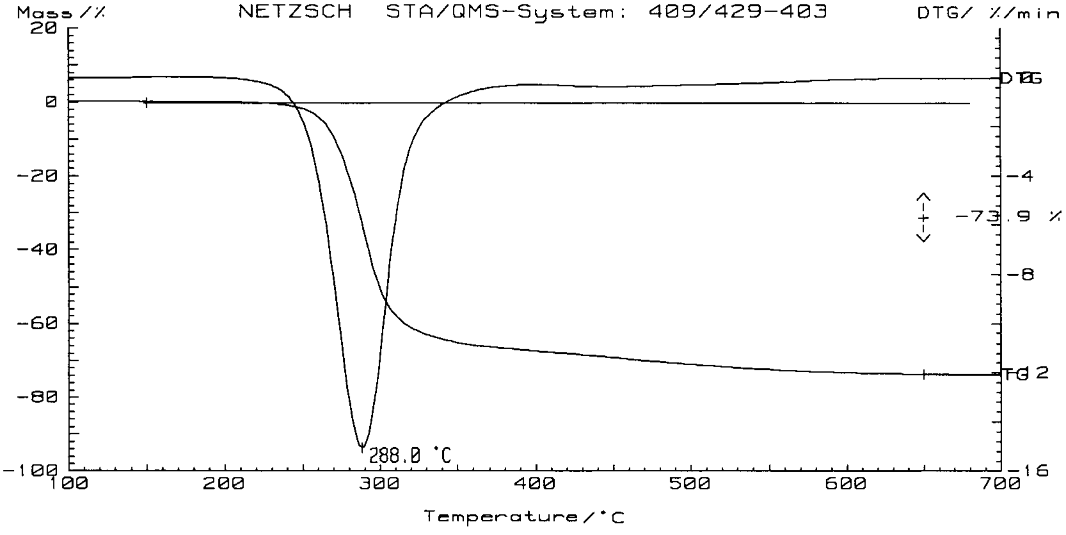

Fig. 2. TG- and DTG-curves of CPVC (66% chlorine content).

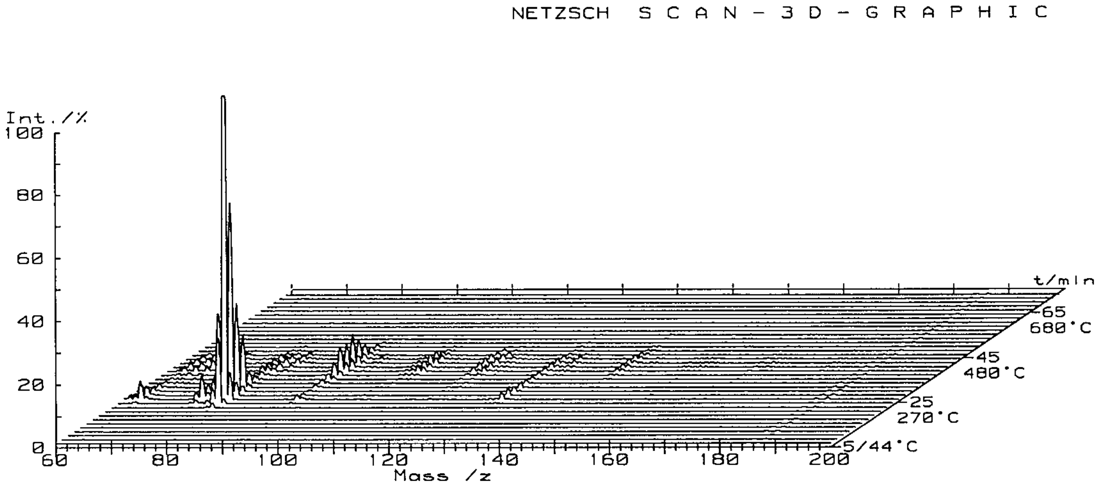

Fig. 3. 3-D scan overview: PVC sample, 57% Cl^- content.

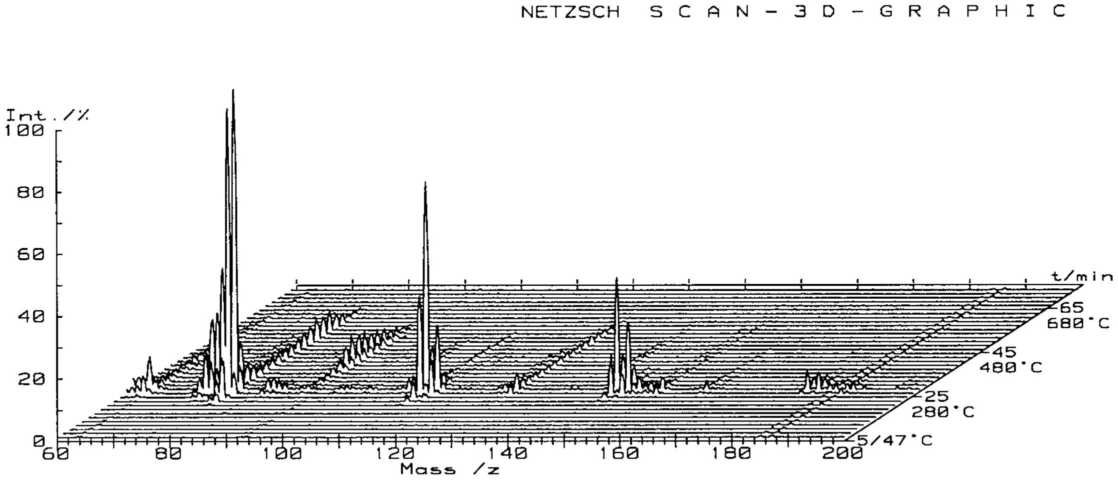

Fig. 4. 3-D scan overview: CPVC sample, 66% Cl^- content.

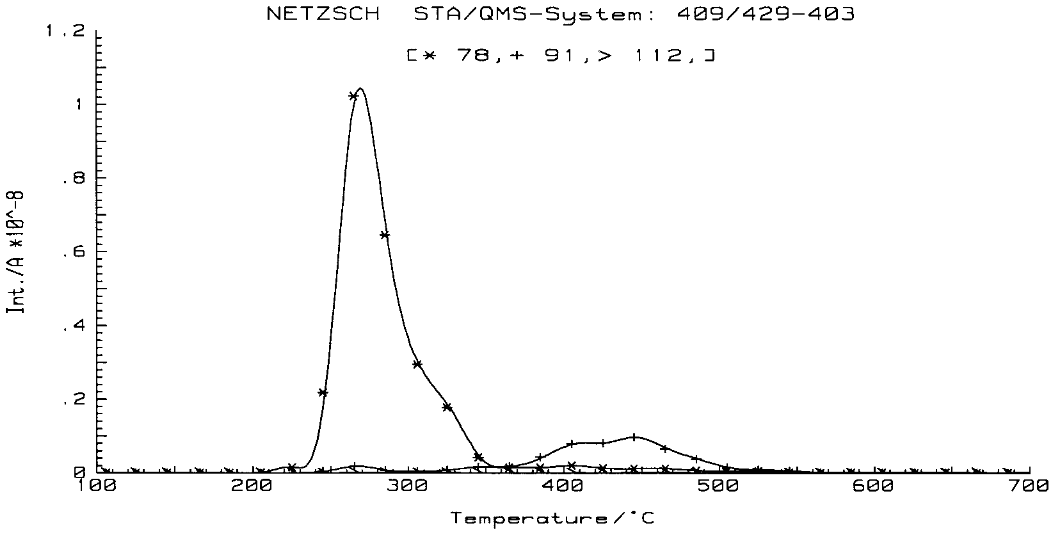

Fig. 5. Temperature-dependent evolution of benzene, tropyllium and benzenechloride from PVC, 57% Cl$^-$ content.

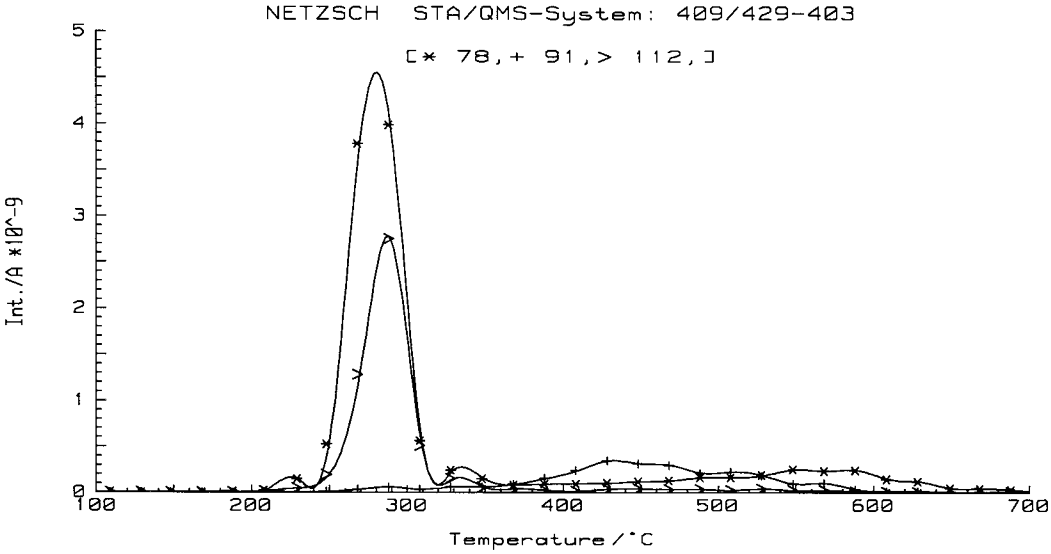

Fig. 6. Temperature-dependent evolution of benzene, tropyllium and benzenechloride from CPVC, 66% Cl$^-$ content.

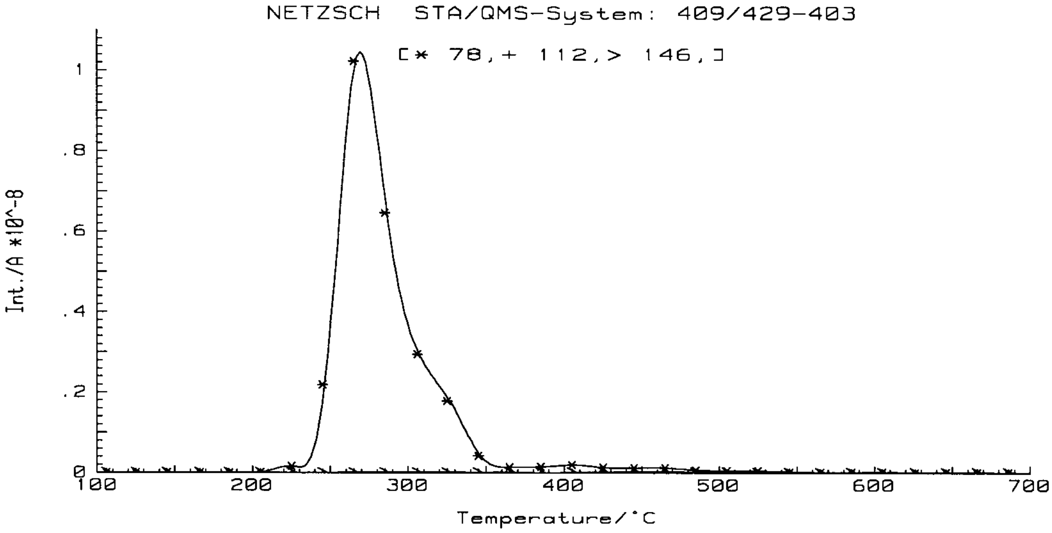

Fig. 7. Temperature-dependent evolution of benzene, benzenechloride and benzenedichloride from PVC, 57% Cl$^-$ content.

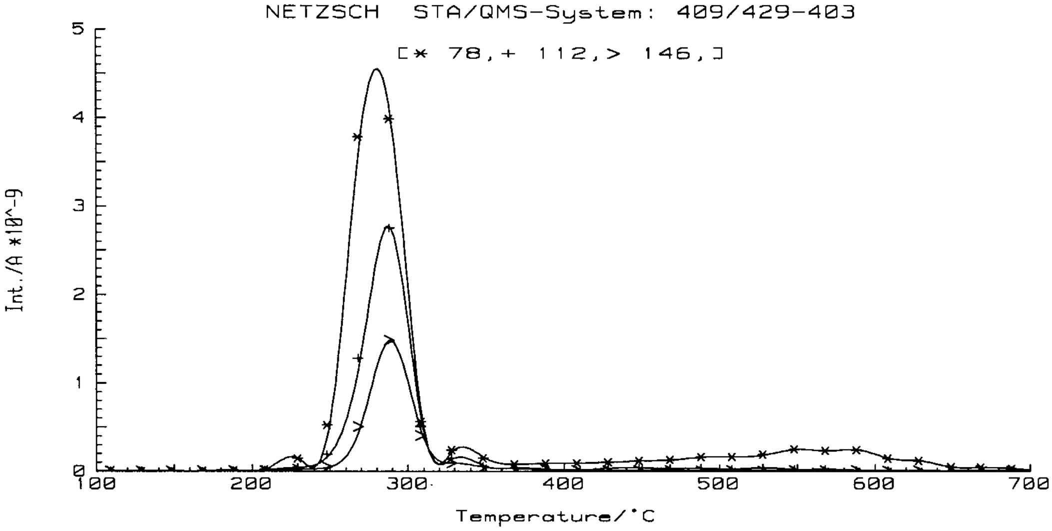

Fig. 8. Temperature-dependent evolution of benzene, benzenechloride and benzenedichloride from CPVC, 66% Cl$^-$ content.

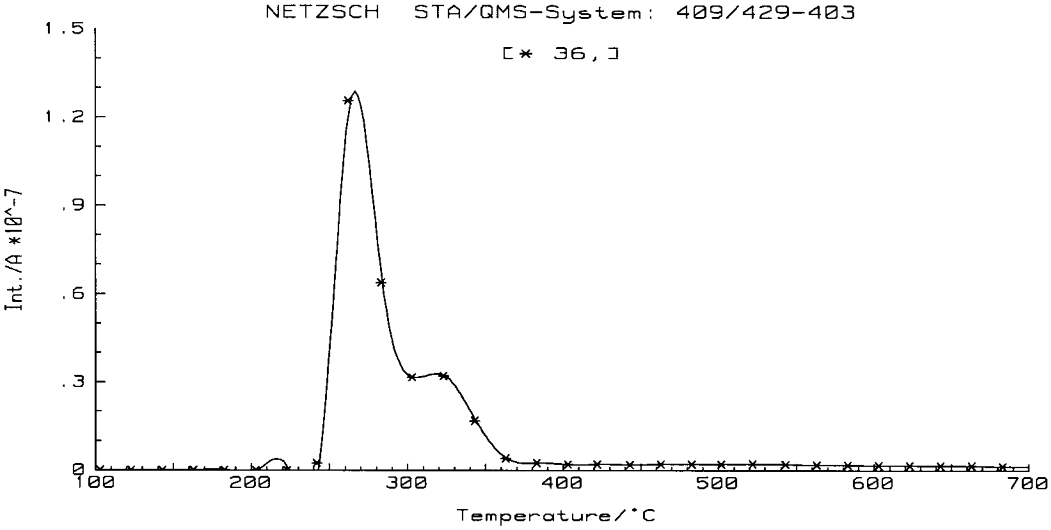

Fig. 9. Temperature-dependent evolution of HCl from PVC, 57% Cl^- content.

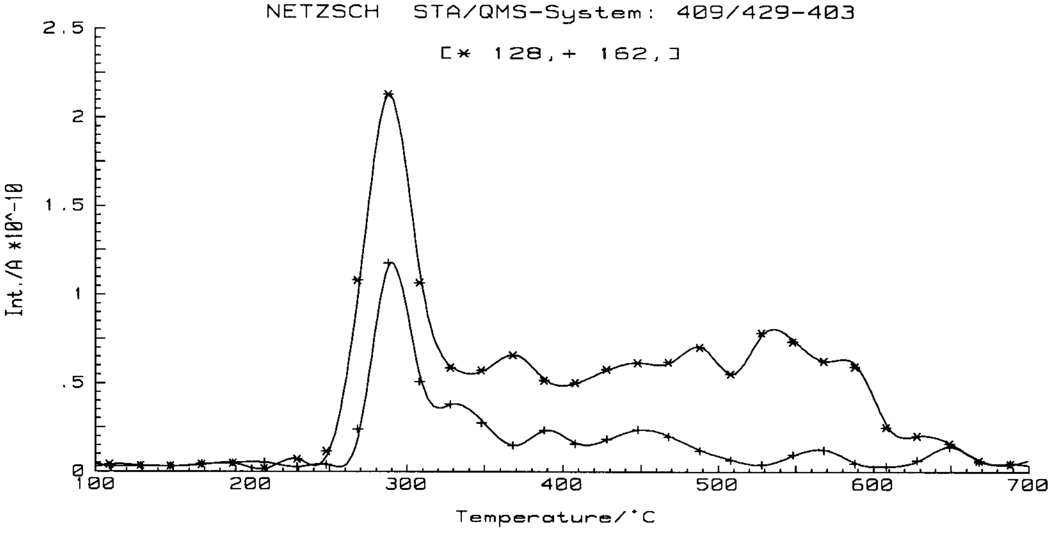

Fig. 10. Temperature-dependent evolution of naphthalene and naphthalenechloride from CPVC, 66% Cl^- content.

Acknowledgements

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References

[1] H. Utschick, M. Ritz, H.-J. Mallon, M. Arnold, W. Ludwig, A. Kettrup, G. Matuschek, J. Cyrys, Thermochim. Acta 234 (1994) 139–151.