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Investigations on the thermal degradation of post-chlorinated polyvinyl chloride[1]

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Abstract

PVC and post-chlorinated PVC have been investigated with respect to their thermal degradation by means of thermogravimetry, mass spectroscopy coupled to thermogravimetry and pyrolysis gas chromatography. The results of these methods are correlated and discussed.

INTRODUCTION

Polyvinyl chloride (PVC) is still produced in abundance because of its broad applicability [1]. By post-chlorination of PVC, products are obtained which are more stable on heating, so increasing the field of applications. Both the ability to recycle and toxicological problems were motivations for investigating the thermal degradation of these products.

The degradation behaviour of PVC has been described in many publications; see, for example, Wiebold et al. [2], Ellinghorst and Hummel [3] and Behnisch et al. [4]. This degradation takes place under inert conditions in two steps; the first step is mainly the dehydrochlorination reaction. In a second step both aliphatic and aromatic hydrocarbons are formed from the residuary double bond-containing chain. Mostly these results were obtained using only one method of investigation. From our

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[1] Dedicated to Hans Georg Wiedemann.

point of view the decomposition reaction is much more complex and various complementary analytical techniques are necessary. There are only few publications regarding the decomposition of post-chlorinated PVC, for example that of Tsuge et al. [5].

EXPERIMENTAL

For our tests we selected three types of PVC, differing in molecular weight and porosity. The PVC was treated with dry chlorine during UV irradiation. The progress of the chlorination was controlled every hour by the determination of chlorine content within the polymer. Products with a chlorine content of 63% were chosen for further investigation. The chlorine content of the polymers was determined by digestion according Schöniger [6] and subsequent coulometric titration.

The molecular weights were determined by size exclusion chromatography (SEC) in tetrahydrofuran solution.

Both the cumulative pore volume and the specific surface area were measured by mercury porosimetry. The resulting data are summarized in Table 1.

The glass transition temperature of the starting and the post-chlorinated materials was determined by means of a differential scanning calorimeter (type DSC 7) under analogous conditions (heating rate 10 K min^{-1}, mass about 10 mg).

The investigations of the thermal decomposition of the polymers were carried out by thermogravimetry (mass 10 mg, rinsing gas argon, heating rate 10 K min^{-1}). In some cases the compositions of the volatile degradation products were analysed by directly coupled mass spectroscopy.

TABLE 1

Data for the PVC types and their post-chlorinated products

Sample number	Cl content/mass%	K	$\overline{M_w}$/g mol^{-1}	$\overline{M_n}$/g mol^{-1}	Cumulative volume/mm^3 g^{-1}	Specific surface area/m^2 g^{-1}
1.0	56.6	65	102100	50000	301	13.9
2.0	56.9	58	60200	30800	396	11.2
3.0	56.6	58	74100	47700	242	13.0
1.1	63.0		98600	48300		
2.1	63.3		72900	34000		
3.1	63.0		67600	34000		
1.2	66.9		107100	53400		

Analogous samples were investigated by pyrolysis gas chromatography (Curie point pyrolysis, 4 s, 500°C, carrier gas argon).

RESULTS AND DISCUSSION

The porosity values of the different types of PVC (1.0; 2.0; 3.0) listed in Table 1 influence the time dependent course of the UV-stimulated chlorination (Fig. 1). Types 1.0 and 2.0 reach high chlorine contents rapidly; in contrast PVC 3.0 has a lower chlorine content even after 10 h chlorination.

As expected, the glass transition temperatures T_g of the chlorinated products of types 1.0 and 2.0 PVC increase with growing chlorine content (Fig. 2), but the T_g values of chlorinated products of the type 3.0 PVC increase only slowly. We believe that (because of the low porosity of the material) there are parts in the polymer which do not react during chlorination, which means that there are high and low chlorinated domains in the product. Therefore the T_g value of pure PVC was measured. Highly chlorinated regions of PVC in a matrix of low chlorine content are not recognizable by DSC measurements.

The slightly different glass transition temperatures of the starting PVC types refer to their different molecular weights. Thermogravimetric investigations of the PVC samples in inert atmosphere show no significant differences in the decomposition properties in spite of their different

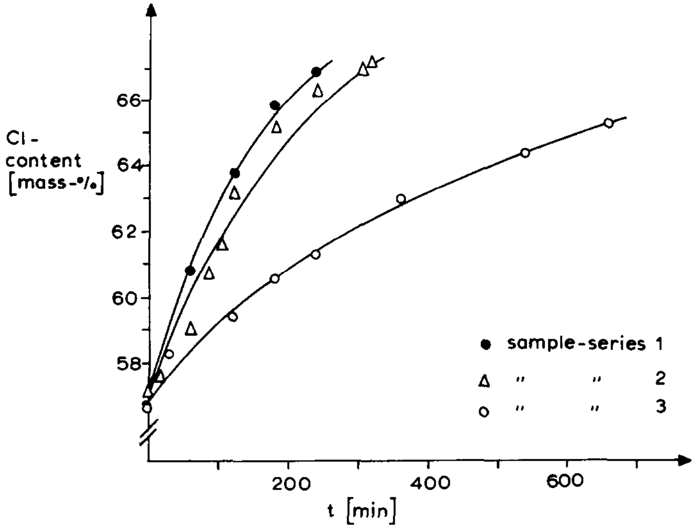

Fig. 1. Time–turnover diagrams of the dry chlorination for three selected PVC samples.

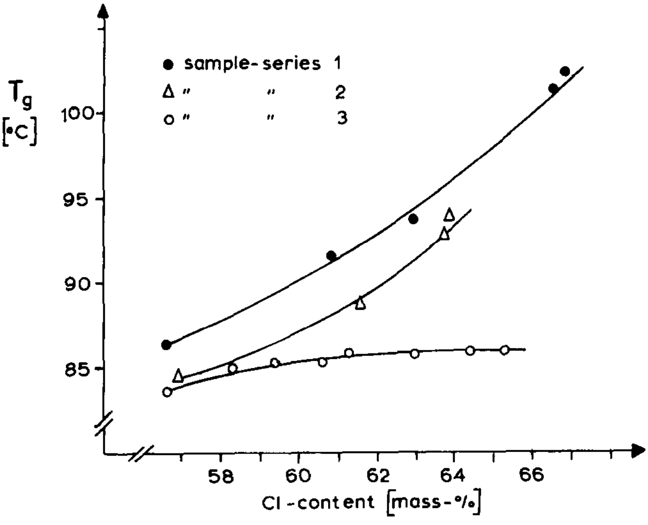

Fig. 2. Glass transition temperatures T_g versus chlorine content of the chlorinated products.

molecular weights and their different porosities; they yield the expected two-step mechanism of the mass loss.

Samples 1.1, 2.1 and 3.1 obtained from samples 1.0, 2.0 and 3.0 by post-chlorination show different decomposition behaviour in their TG curves in spite of having the same chlorine content (cf. Figs. 3 and 4).

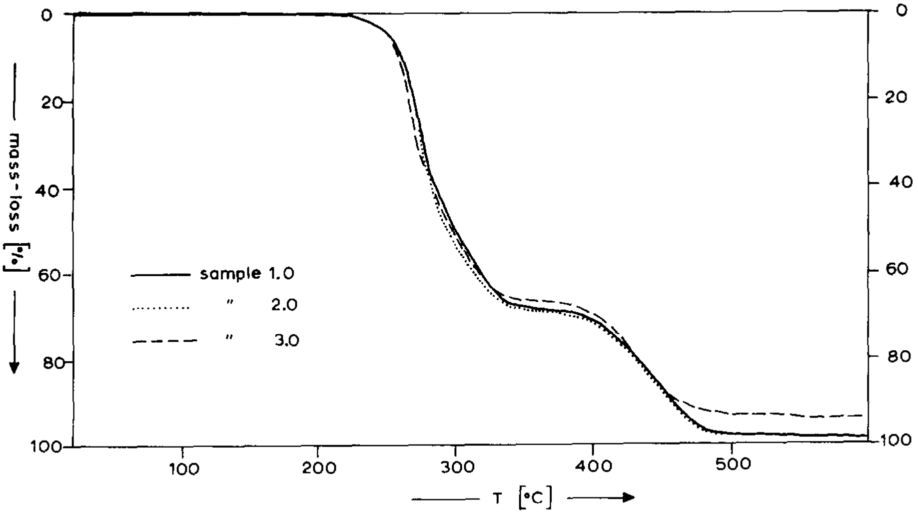

Fig. 3. TG curves of the PVC starting material.

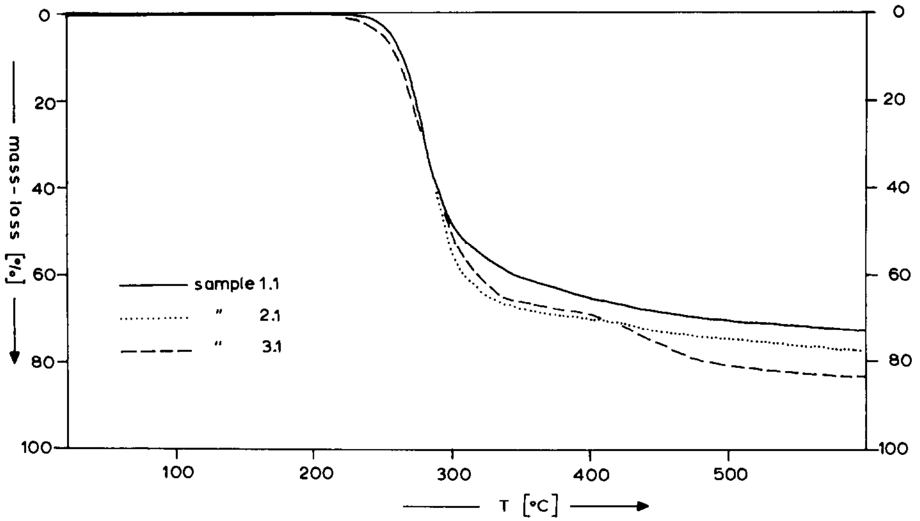

Fig. 4. TG curves of the post-chlorinated products with a chlorine content of 63 mass%.

Indeed the decomposition reaction starts at nearly the same temperature as the parent PVC, but is essentially a one-step reaction and yields distinctly larger amounts of residues. Moreover a relationship with the chlorinating behaviour of the PVC types is detectable (Fig. 1). Obviously this is an indication of the homogeneity of chlorine substitution in the polymer: higher quantities of unchlorinated PVC sequences lead to decomposition behaviour similar to that of the PVC, which means it leads to larger amounts of residues. Samples 1.1 and 2.1 had very similar residues, whereas the residue of sample 3.1 is significantly smaller. These findings are shown in Fig. 2. Thus the thermoanalytical investigation permits statements to be made about the homogeneity of the chlorine distribution in the chlorinated PVC.

Simultaneous thermogravimetric and mass spectroscopic measurements were carried out on the sample series 1.0, 1.1 and 1.2. The TG curves, and especially the DTG curves, (Fig. 5) show the decrease of the second step of the thermal decomposition with increasing chlorine content. The mass loss of the first step results mainly from the dehydrochlorination reaction, confirmed by mass spectroscopy (mass number 36, Fig. 6). An unsaturated chain remains as residue. Depending on the chlorine content of the polymer the residue contains different amounts of chlorine (at 380°C: product 1.0, 0% Cl; product 1.2, 9% Cl).

The further thermal decomposition of this chain proceeds substantially more slowly and is characterized by formation of aromatics, or in the case

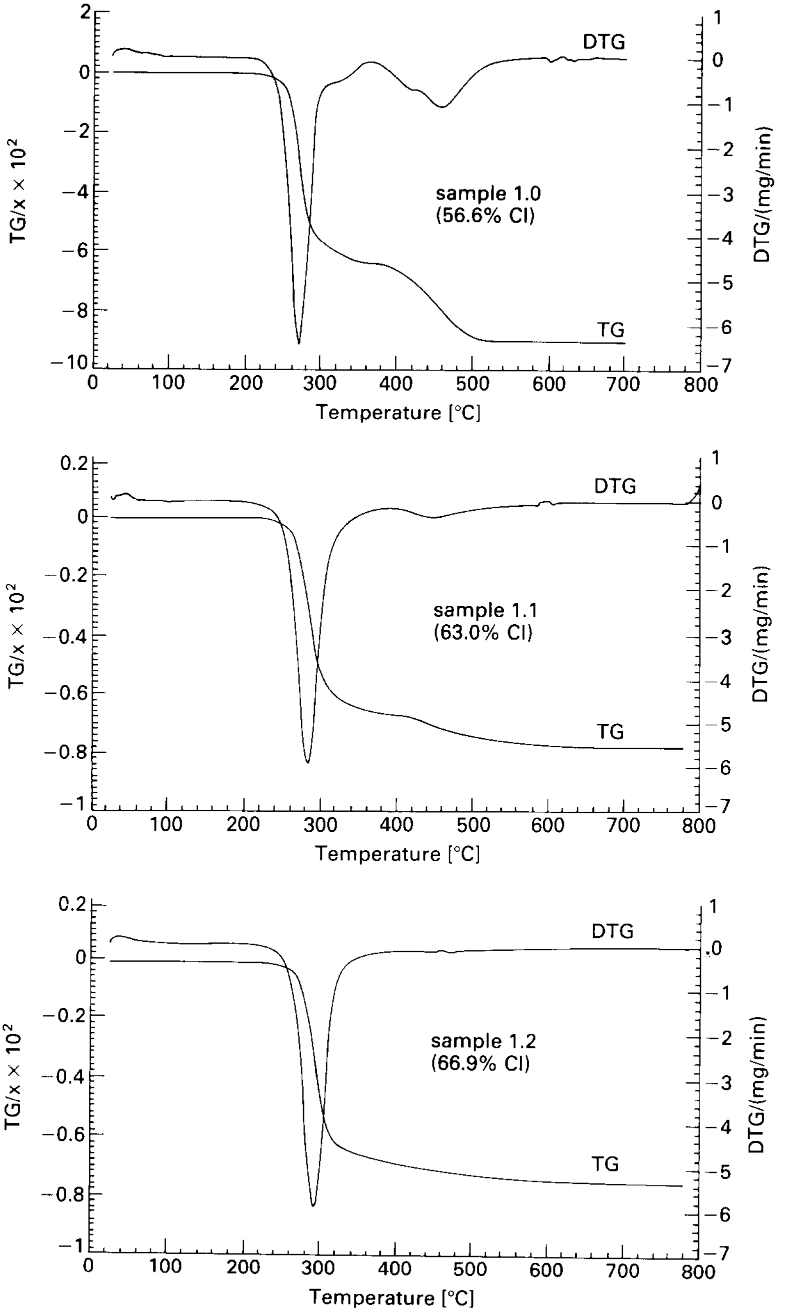

Fig. 5. TG and DTG curves of samples series 1 with various chlorine contents.

of post-chlorinated PVC of chlorinated aromatics and short-chain aliphatics. This process begins in the course of dehydrochlorination so that, besides hydrogen chloride, volatile hydrocarbons arc formed. This can be seen in the mass spectrograms at 300°C (Fig. 7), in which the formation of

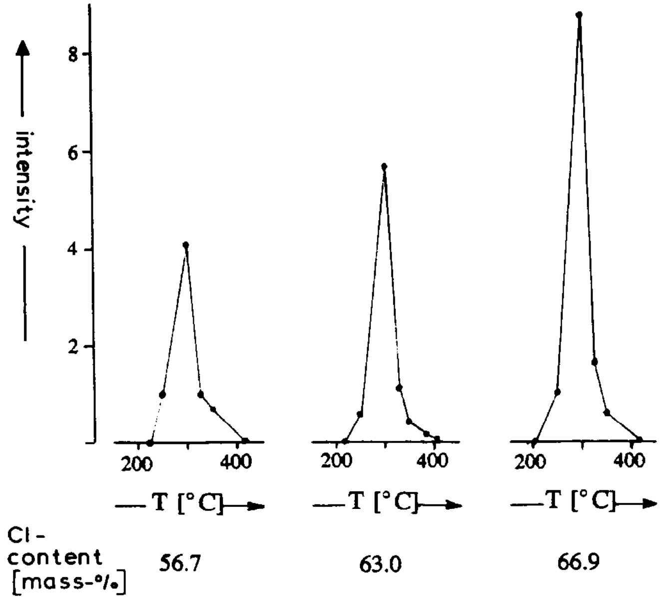

Fig. 6. Mass spectroscopic intensities of the decomposition product HCl (mass number 36) in the course of dehydrochlorination.

benzene in the case of higher colorinated product decreases in favour of the formation of chlorinated aromatics.

The disappearance of the second TG step is the result of the higher thermal stability of the decomposition residue at 300°C with increasing chlorine content.

Above 300°C the thermal decomposition of the polymer chain takes a non-uniform course with regard to the quality and quantity of the decomposition products formed. At the beginning (i.e. at 300°C) benzene and chlorinated aromatics are formed preferentially. The formation of toluene mainly takes place at about 450°C but decreases with increasing chlorine content of the starting polymers (Fig. 8).

Figure 7 shows that at about 300°C the spectrum of volatile decomposition products depends on the chlorine content of the polymer. The amount of benzene decreases but the amounts of chlorobenzene and dichlorobenzene (Fig. 9) increase with the degree of chlorination. The formation of dichlorobenzene has its maximum at 300°C (Fig. 10). Obviously this process takes place in the temperature range 200–400°C, i.e. simultaneously with dehydrochlorination. Especially in the case of non- or low chlorinated products this is visible in the unusual splitting of the DTG peak in the temperature range 310–360°C (Fig. 5).

The thermal decomposition of the polymers is essentially finished at

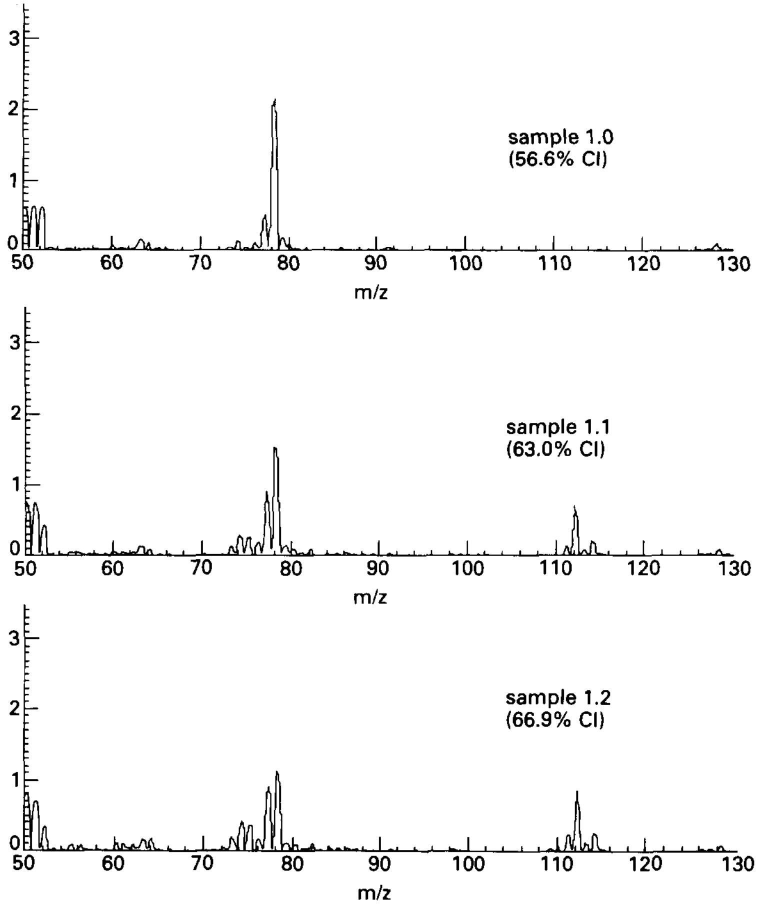

Fig. 7. Mass spectroscopic intensities in the range of benzene and chlorobenzene (mass numbers 78 and 112) at 300°C.

500°C as our investigations verify. Therefore we selected a temperature of 500°C for the Curie-point-pyrolysis. In contrast to the Tg and MS tests, for pyrolysis-GC studies the heating of the sample needs only milliseconds. Despite this essential difference of these methods we obtained comparable results.

Table 2 gives a review of the pyrolysis products obtained; the substances vinylidene chloride, naphthalene, chloronaphthalene, biphenyl and the tetrachlorobenzenes are not named. Benzene is the main component of the PVC pyrolysis products, whereas chlorinated aromatics are not detectable. Regarding the toluene content, the differences refer, from our point of view, to different degrees of branching of the polymer in question. This is verified by the different degrees of branching obtained from SEC measurements: PVC 1.0, 3 side-chains/polymer chain; PVC

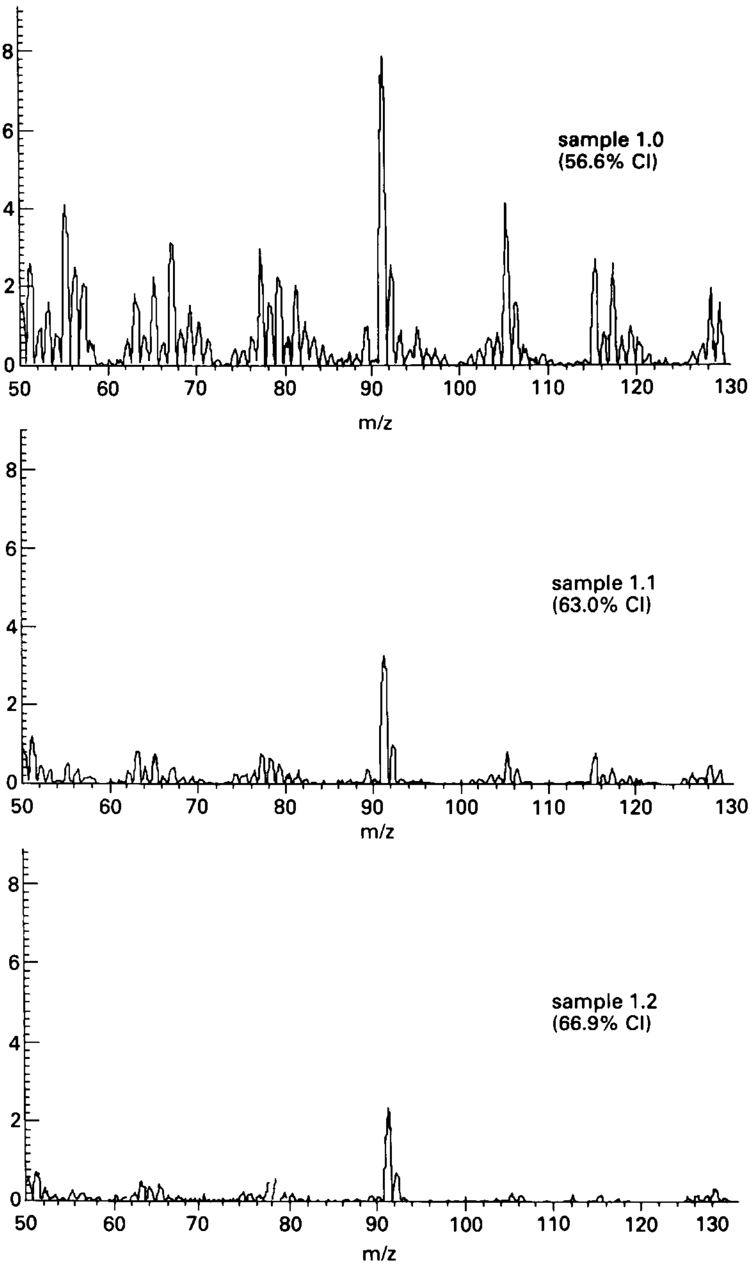

Fig. 8. Mass spectroscopic intensities in the range of toluene (mass number 91) at 450°C.

2.0, <1 side-chains/polymer chain; PVC 3.0, 15 side-chains/polymer chain.

Significant differences with reference to the composition of the pyrolysis product could be determined in the case of post-chlorinated PVC. In spite

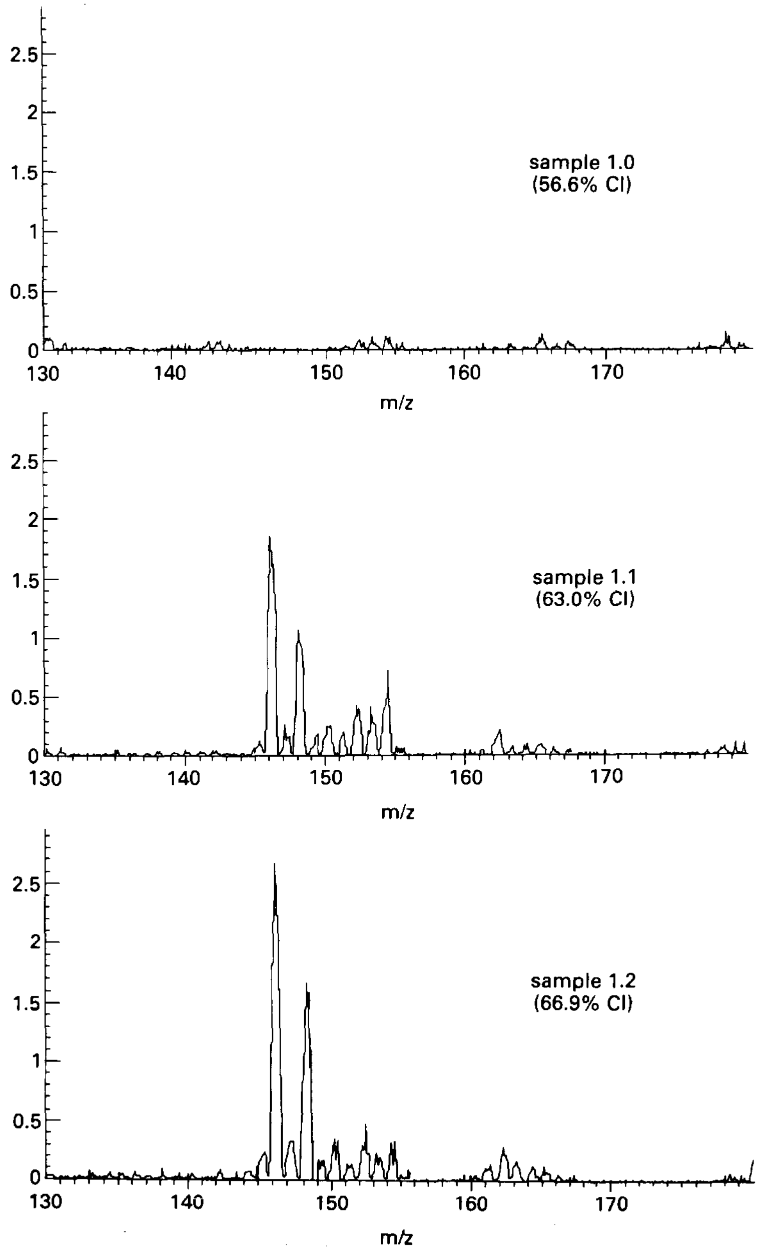

Fig. 9. Mass spectroscopic intensities in the range of dichlorobenzene (mass number 146) at 300°C.

of the same chlorine content the benzene, chlorobenzene and dichlorobenzene portions differ considerably. Large benzene portions lead to the conclusion that the investigated sample contains rather long non-postchlorinated sequences, whereas simultaneously due to the higher chlorin-

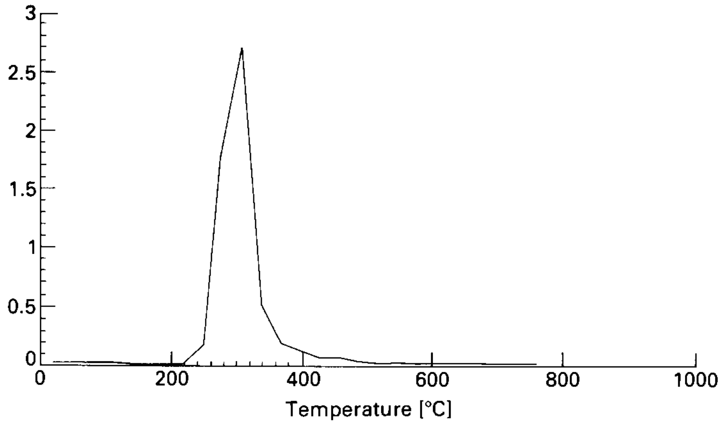

Fig. 10. Mass spectroscopic intensities of dichlorobenzene (mass number 146) versus temperature for sample 1.3.

ated sequences larger portions of di- and trichlorobenzene were detected. Product 3.1 shows this behaviour. It is inhomogeneously chlorinated because of the lower porosity of PVC 3.0 and the consequent bad accessibility of chlorine to the material. This corresponds to the low chlorination rate (Fig. 1) and the weak dependence of the glass transition temperatures on chlorine content (Fig. 2). Obviously products 1.1 and 2.1 are chlorinated more homogeneously. This is also evident from the lower benzene but higher chlorobenzene content compared with that of the product 3.1. In this way it is shown that a high chlorination rate (Fig. 1) leads to a more homogeneous distribution of the introduced chlorine. As can be seen the porosity of the starting PVC is of great importance relative to the result of chlorination. As expected higher chlorination of the product yields a further decrease of the benzene portion in favour of tri- and tetrachlorobenzene as is evident from the product 1.2. The occurrence of higher chlorinated aromatics besides benzene confirms that the chlorination not only consists of substituting CH_2– groups but also of simultaneous chlorination of CHCl groups in the formation of 1,1-chlorine substituted structures in post-chlorinated PVC.

The reduction of the toluene portion in the pyrolysis product of the post-chlorinated samples compared to the starting material is remarkable. It points to a reduction of branching during the chlorination process. The decrease of the toluene portion correlates with the degree of branching in the starting material. The same tendency is also visible from the molecular masses M_w and M_n of the samples in question (Table 1).

TABLE 2

Pyrolysis gas chromatography results in mass%

Sample number	Cl content/mass%	Benzene	Toluene	Cl-benzene	*m*-DCB	*p*-DCB	*o*-DCB	1,3,5-TCB	1,2,4-TCB	1,2,3-TCB
1.0	56.6	71.8	2.0	0	0	0	0	0	0	0
2.0	56.9	70.7	1.7	0.2	0	0	0	0	0	0
3.0	56.6	70.7	2.2	0.2	<0.1	<0.1	<0.1	0	0	0
1.1	63.0	51.6	1.5	20.9	2.1	1.8	2.0	0.1	0.5	0.2
2.1	63.3	48.5	1.3	21.1	2.6	2.3	2.6	0.1	1.0	0.3
3.1	63.0	55.6	1.2	15.5	2.8	2.5	2.5	0.4	1.7	0.4
1.2	66.9	42.8	0.6	31.0	4.5	3.8	4.0	0.4	1.3	0.4

Key: Cl-benzene, chlorobenzene; *m*-, *p*-, *o*-DCB, *meta*-, *para*-, *ortho*-dichlorobenzene; 1,3,5-, 1,2,4-, 1,2,3-TCB, 1,3,5-, 1,2,4-, 1,2,3-trichlorobenzene.

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