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Note

INVESTIGATION OF THE THERMAL DEGRADATION OF AN HET ACID CONTAINING UNSATURATED POLYESTER RESIN BY FLASH PYROLYSIS IN A MASS SPECTROMETER

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In a previous study [1,2], the primary products of thermal degradation of polyesters containing the HET acid moiety (1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic acid) were analyzed by a GC/MS technique. From these studies the reaction mechanisms of the primary processes of thermal degradation could be established and consequently, some knowledge regarding the mechanism for flame retardancy by the HET moiety in these particular systems was obtained.

The techniques applied hitherto, however, were not suitable for observing unstable intermediates in the course of degradation, e.g., radicals, which are assumed to show much more vividly the primary steps occurring in the system. For this reason flash pyrolysis experiments were performed directly in the mass spectrometer.

EXPERIMENTAL

An unsaturated polyester consisting of fumaric acid, HET acid and butanediol [1,4] in a molar ratio of 1 : 1 : 2.2 was prepared, to which 43 phr of styrene were added along with 1% by weight of dibenzoylperoxide as curing agent. Two μl of the polyester resin were placed on a platinum ribbon probe (Hewlett-Packard model 18850 pyrolyzer) in each experiment and cured directly on the ribbon at 110°C for 1 h. For pyrolysis experiments the ribbon was situated in the mass spectrometer (Balzers model QMG 511) at a distance of approximately 5 cm from the ion source. The samples were pyrolyzed at end temperatures of 400, 600 and 800°C, respectively, for 10 s. A ramp rate of 0.1°C ms^{-1} was applied. During and immediately after pyrolysis mass spectra were recorded with a scan speed of 30 ms per mass unit. Owing to the high suction rate of the diffusion pump the volatiles formed during the course of the experiment did not raise the pressure inside the mass spectrometer above ca. 5×10^{-4} mb.

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Since the mass spectra of the main products of degradation were known, the significant information was obtained from the peaks which did not belong to those products.

RESULTS AND DISCUSSION

Qualitative inspection of the mass spectra during and after pyrolysis showed quite similar peaks at the different temperatures investigated. A few discrepancies, which lead to significant conclusions will, however, be discussed.

The mass spectrum obtained at 400°C immediately after the pyrolysis experiment is shown in Fig. 1, and is discussed briefly in Table 1. Conclusions based upon the evaluation of the mass spectra are summarized below.

It is remarkable that even under conditions of high vacuum secondary reactions besides the primary fragmentation reactions can be observed. This suggests that these reactions may have taken place already in the degrading polymer matrix. It is, however, conceded that in the vicinity of the platinum ribbon probe a higher local concentration of volatiles is to be expected than is indicated by the pressure gauge.

The formation of HCl reflects the contribution of flame poisoning reac-

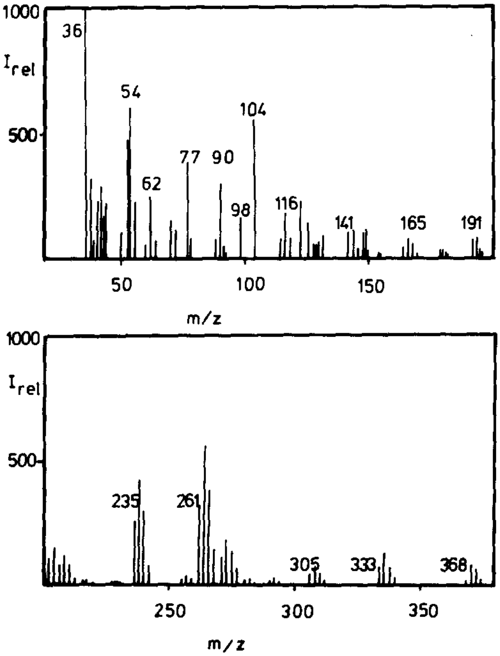

Fig. 1. Mass spectrum of the unsaturated polyester resin pyrolyzed at 400°C, after pyrolysis. Mass range under consideration, 35–400. No quantitative statements should be made from the intensities.

TABLE 1

Discussion of the mass spectrum from Fig. 1

m/z	Interpretation and remarks
36, 38	HCl, indicates transfer reactions from the chlorinated product
39–42	C_3H_3, C_3H_5, C_3H_6, not specific
44	CO_2, due to decarboxylation
53, 54	Butadiene from the butanediol moiety
55	$CH_2CHCH_2CH_2\cdot$, known in butyl esters
56	Butene
60	C_5 from hexachlorocyclopentadiene
62, 64	$CHClCH_2\cdot$
70, 72	Cl_2, dihydrofuran, tetrahydrofuran
77, 78	Benzene, at higher temperatures of pyrolysis $m/z = 76$ becomes dominant, indicating the real occurrence of radicals ($C_6H_6 - x$ H, $x = 1$ or 2)
90,91,92	Toluene (radical) cf. $m/z = 77$
98	Maleic anhydride, retro-Diels–Alder reaction of the HET moiety and further due to isomerization of fumaric acid and water release
104–106	Broad, styrene and ethylbenzene
114	Fumaric acid $-2H\cdot$ or methylsuccinicanhydride from fragmentation of styrene/fumaric acid copolymer
116	Fumaric acid
118	Succinic acid or α-methylstyrene, cf. $m/z = 114$
122	Benzoic acid?
125–129	$C_4H_7Cl_2\cdot$, transfer of Cl_2 to a fragment from butanediol, isotopic pattern fits Cl_2
131	Broad, adduct of butadiene and benzene radical
141–145	C_3Cl_3 from hexachlorocyclopentadiene
153	Broad, biphenyl (radical) from recombination of benzene radicals
165–169	C_5Cl_3 from hexachlorocyclopentadiene
178–180	Broad, stilbene from recombination of $m/z = 90$
191–195	$C_4H_3Cl_4\cdot$ chlorine transfer to C_4 (butanediol fragment) or rather H transfer to a fragment from hexachlorocyclopentadiene
201–209	C_5HCl_4, H transfer to the tetrachlorocyclopentadienyl entity
226–230	Terphenyl (radical) *o*-isomer fits best the pattern, c.f. ref. 4
235	pentachlorocyclopentadienyl radical
254–258	$m/z = 289 - Cl\cdot$
261–267	Pentachloronorbornadienyl cation cf. ref. 3.
270–276	Hexachlorocyclopentadiene
279–283	$m/z = 305 -$ acetylene
289–293	HET anhydride – Cl and CO_2
333–339	HET anhydride – Cl
368–376	HET anhydride

tions [5], e.g.

$$H\cdot + HCl \rightarrow H_2 + Cl\cdot$$

to achieve flame retardancy in systems containing HET acid. The chlorine radical, which is formed in the first step, is most likely identified as the allylic chlorine in hexachlorocyclopentadiene which is generated by the retro-Diels–Alder reaction of the HET moiety. Also, addition of chlorine to fragments evolved from the butanediol component can be observed. On the other hand, no halogenated aromatics (e.g., chlorobenzene, $m/z = 112$ or benzylchloride, $m/z = 126$) are observed. Therefore, the enhanced formation of ethylbenzene and toluene at the expense of styrene in the presence of the HET moiety in unsaturated polyester resins [1] must be interpreted in terms of an indirect action of the halogen, e.g., $H\cdot$ transfer from HCl or some similar reaction. The formation of dimers and trimers of the benzene radical reflects the high reactivity of these radicals. Besides the flame poisoning reaction, another mechanism of flame retardancy consisting of hydrogen transfer onto the fragments of hexachlorocyclopentadiene to yield less flammable "bounded hydrogen" is suggested. The proposal of such a mechanism is based upon the occurrence of fragments 191 and 201 in Table 1. The hydrogen transfer may occur from free hydrogen radicals, thus interfering with chain branching reactions due to scavenging of these reactive radicals.

The mechanism of polyester chain degradation was not completely clear from previous experiments. One possibility is that the retro-Diels–Alder reaction of the HET moiety takes place with subsequent degradation of the residual maleic acid moiety to yield maleic anhydride and tetrahydrofuran via an unzipping process, or to yield butadiene and the corresponding acid, which loses water. A second possibility is that the HET acid is formed directly in the degradation process. This ambiguity was a consequence of HET acid being converted immediately to the anhydride on the GC column. The mass spectra obtained during pyrolysis in contrast to those obtained after pyrolysis showed a clear peak at $m/z = 386$–392, which is certainly the M^+ peak of HET acid. Based upon the results of these experiments, it could be established that, at least of some extent, the path of degradation in the system under investigation runs via free HET acid.

REFERENCES

1 C.T. Vijayakumar and J.K. Fink, J. Appl. Polym. Sci., 27 (1982) 1629.

2 C.T. Vijayakumar, J.K. Fink and K. Lederer, Angew. Makromol. Chem., 113 (1983) 121.

3 C.T. Vijayakumar and J.K. Fink, Int. J. Mass Spectrom. Ion Phys., 48 (1983) 59.

4 A. Cornu and R. Massot, Compilation of Mass Spectral Data, Heyden, London, 2nd edn., 1975.

5 R.J. Schwarz, in W.C. Kuryla and A.J. Papa (Eds.), Flame Retardancy of Polymeric Materials, Dekker, New York, 1973, p. 102.