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Chlorinated Products of Plastic Pyrolysis

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Abstract: The formation of various chlorinated products in pyrolysis of polymers and plastics additives was studied. Formation of chlorobenzenes (in addition to the monomers) from poly(chlorostyrene) and poly(vinylbenzyl chloride) was observed. Hydrogen chloride is only produced from these polymers at above 600 °C when the chlorine atoms are cleaved off and abstract hydrogen. A similar process takes place in aromatic chlorine-containing dyes, in which the strong aromatic molecular structure prevents the thermal cleavage of chloroaromatic volatile products. We have observed that cupric and ferric chlorides chlorinate phenolic thermal decomposition products of plastic materials which originate either from the polymer or from the stabilizer. The highest yields of chlorophenols are obtained in pyrolysis at around 700 °C.

INTRODUCTION

Chemical recycling of plastic materials often involves pyrolysis or thermally assisted reactions. One of the potential hazards of the high-temperature management techniques for polymers is the formation of chlorinated aromatic hydrocarbons (Refs. 1-3). Poly(vinyl chloride), poly(vinylidene chloride) and poly(chloroprene) are known sources of hydrogen chloride and chlorobenzenes in thermal decomposition (Refs. 4,5). Poly(chlorostyrene), poly(bromostyrene) and poly(vinylbenzyl chloride) decompose by heat mainly to monomer: chlorostyrene, bromostyrene and vinylbenzyl chloride, respectively (Refs. 6-8). However, not only pyrolysis of chlorinated polymers may result in chloroaromatic volatile products. It was noticed by Eklund et al. (Ref. 9) that phenol and HCl at 550 °C yield a large variety of chlorinated toxic compounds. Since chlorobenzenes and chlorophenols are considered as precursors in the formation of chlorinated dioxins and dibenzofurans in flame chemistry (Ref. 10), their probable formation merits attention. We have observed earlier that some of the polyethylene pyrolysis products are chlorinated by cupric and ferric chloride (Ref. 11). Iron and copper are frequently present in polymer products; moreover, their compounds are often used as smoke retardants (Refs. 12,13). These metals may form chlorides under the conditions of pyrolysis (Ref. 13). Additives could be also precursors of toxic substances, e.g., a bromodiphenyl ether-based flame retarder proved to be transformed to bromodioxin under pyrolysis (Ref. 14).

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The aim of this work is to define some typical ways of chlorine-containing aromatic product formation from plastics in the temperature range from 500 to 800 °C. Chlorine-containing polymers and organic dyes are investigated as sources of chloroaromatic products on one hand, formation of chlorophenols in the presence of ferric and cupric chlorides, pyrolyzed together with polymers and additives releasing phenols on the other.

RESULTS AND DISCUSSION

Chloroaromatic polymers

A polymer built up from chloroaromatic monomers is considered as an obvious origin of chloroaromatic volatile compounds. A more detailed investigation of poly(chlorostyrene) in the temperature range of 500-800 °C revealed that chloronaphthalenes, chlorophenanthrenes and chloropyrenes are also formed in addition to the monomers. The pyrograms of poly(chlorostyrene) obtained at 600 and 700 °C are compared in Fig. 1.

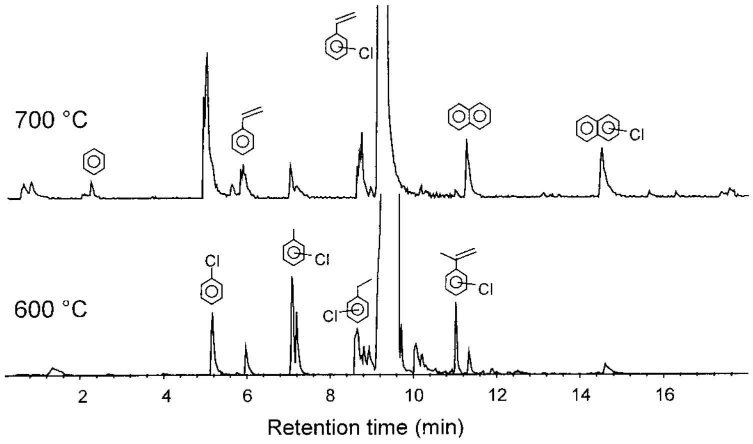

Fig. 1. Gas chromatograms of the products from poly(chlorostyrene) pyrolyzed at 600 and 700 °C. (The monomer peaks are outside the figure due to the fivefold magnification of the intensity scale)

The increased importance of chlorobenzene at 700 °C indicates that the scission of side groups becomes more significant at above 600 °C. Compounds formed through the cleavage of chlorine from the aromatic ring, such as styrene and benzene, are also observed at above 600 °C. Chloronaphthalenes and further chlorinated fused aromatic hydrocarbons are formed admittedly through the cyclization and aromatization of the chain fragments having lost side groups. Though of less importance, these reactions are also included in the thermal decomposition scheme in Fig. 2.

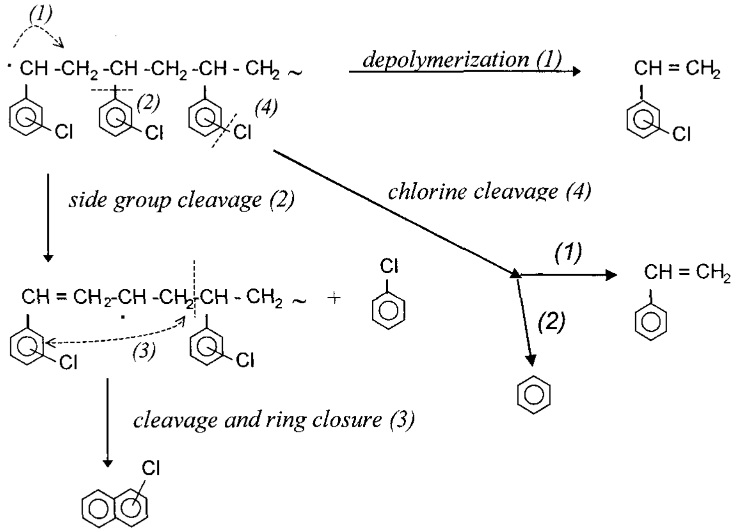

Fig. 2. Thermal decomposition scheme of poly(chlorostyrene)

In Fig. 3a, the formation curves of some characteristic volatile products monitored by direct probe pyrolysis show that the side group scission and chlorine cleavage occur in the same temperature range. Chloronaphthalene is formed at somewhat higher temperatures. Formation of hydrogen chloride suggests that the cleaved chlorine atom also abstracts hydrogen from the polymer chain. In Fig. 3b, the hydrogen chloride ion curves for poly(chlorostyrene) and poly(vinylbenzyl chloride) are compared. Hydrogen chloride evolves in a lower temperature range for the latter, obviously because the chlorine cleavage is easier from the benzylic carbon than from the aromatic carbon of chlorostyrene.

Chloroaromatic organic dyes

In the pyrograms of a Dioxazine Violet 23 concentrate in high-density polyethylene, two chlorine-containing products were identified: hydrochloric acid and 1,2-dichlorobenzene. 1,4-Dichlorobenzene was not found, probably because the central moiety of the dye molecule shown in Fig. 4 is firmly bound by four bonds in a symmetric conjugated arrangement. 1,2-Dichlorobenzene could be derived from a side product of the dye synthesis with asymmetric position of chlorine atoms, which polarizes and lowers the stability of the central moiety of the molecule shown at the bottom of Fig. 4. The succession of the ion curves of the direct probe pyrolysis shown in the figure indicates that chlorine cleavage in the dye molecule leading to hydrogen chloride preceded the formation of 9-ethyl-2-hydroxycarbazole.

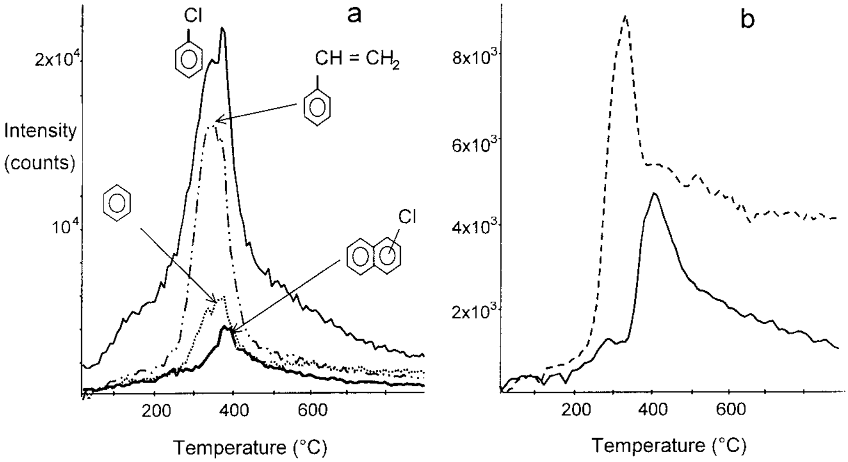

Fig. 3. MS ion curves of side-group scission and chlorine cleavage products in pyrolysis of polymers: (a) poly(chlorostyrene), (b) hydrogen chloride ion curves for poly(chlorostyrene) (full line) and poly(vinylbenzyl chloride) (dashed line)

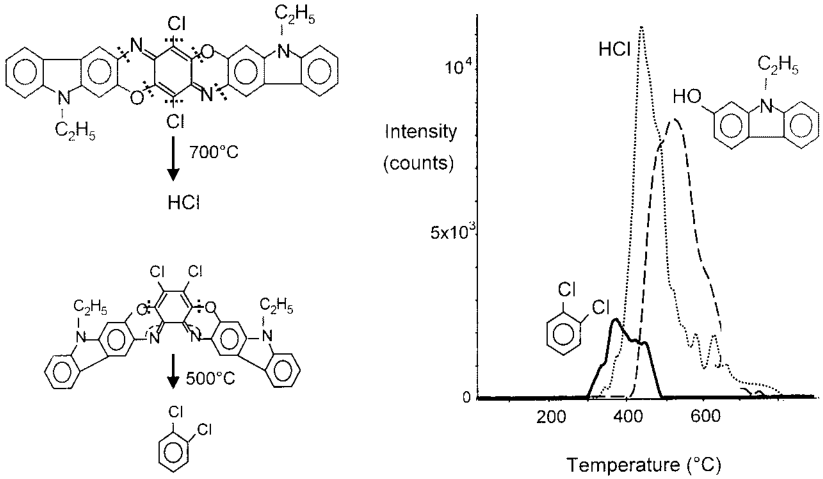

Fig. 4. Scheme of HCl and dichlorobenzene formation from Dioxazine Violet and MS ion curves of the volatile products from pyrolysis of Dioxazine Violet

Pyrogram of a Tetrachloroisoindolinone Yellow concentrate in polyethylene contains a series of chloroaromatic products. Their mass chromatograms are shown in Fig. 5 together with the total ion chromatogram of the 700 °C pyrolyzate. All of the identified chloroaromatic compounds are formed through the cleavage of the isoindolinone ring giving the nitrile group. The thermal decomposition reactions of this yellow dye are schemed in Fig. 6. Abundant formation of hydrogen chloride as well as of trichloro- and dichlorobenzonitrile at above 700 °C suggest the cleavage of chlorine from the tetrachlorinated aromatic rings.

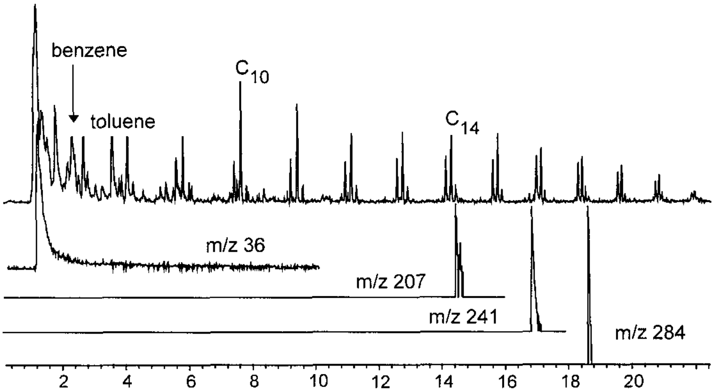

Fig. 5. Pyrogram of Tetrachloroisoindolinone Yellow dye in PE at 700 °C and masschromatograms of hydrogen chloride (m/z 36), trichlorobenzonitrile (m/z 207), tetrachlorobenzonitrile (m/z 241) and tetrachloroisoindolinone (m/z 284)

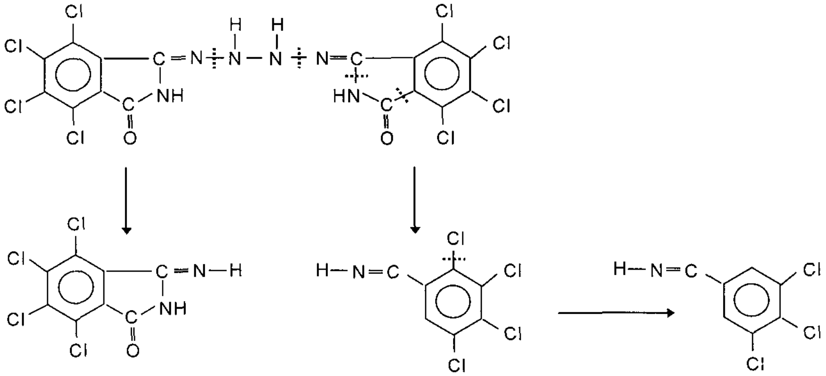

Fig. 6. Thermal decomposition scheme of Tetrachloroisoindolinone Yellow dye

Phthalocyanine pigments are highly stable to heat due to their aromatic ring structure. When pyrolyzing halogenated copper-containing Phthalocyanine Green 36, no chloroaromatic volatile products could be detected. However, chlorine and bromine are cleaved thermally as hydrogen chloride and hydrogen bromide at around 700 °C. The direct probe pyrolysis ion curves for hydrogen halides from Phthalocyanine Green 36 are shown in Fig. 7a.

Comparison of hydrogen chloride ion curves from the three dye concentrates, demonstrated in Fig. 7b, suggests that the chlorine cleavage from aromatic or conjugated carbon occurs in the same temperature range and is not much influenced by the structure of the system.

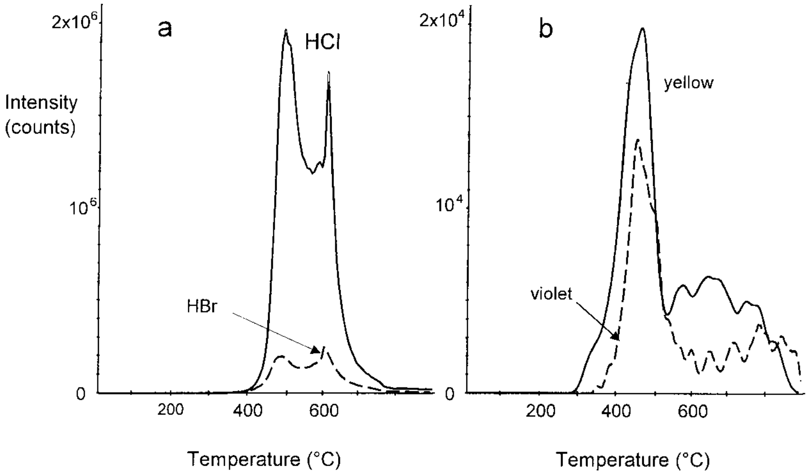

Fig. 7. MS ion curves of HCl and HBr from pyrolysis of halogenated copper-containing Phthalocyanine Green (a) and of HCl from Dioxazine Violet and Tetrachloroisoindolinone Yellow (b)

Chlorophenol formation

GC/MS results revealed that chlorination of phenolic thermal decomposition products occurs when cupric or ferric chloride is present in pyrolysis. Five chlorophenols and one dichlorophenol were identified among the products of a hindered phenolic antioxidant (Irganox 245) pyrolyzed in the presence of Cu(II) chloride at 600 – 800 °C (Ref. 15). Figure 8 shows the 700 °C pyrogram.

2- and 4-chlorophenols, 2,4- and 2,6-dichlorophenols and 2,4,6-trichlorophenol are formed from a phenol-formaldehyde Novolak in the presence of Cu(II) or Fe(III) chlorides. The relative yields of the chlorophenolic products are compared in Fig. 9.

The thermal decomposition of the Bisphenol A moiety of epoxy resin and polycarbonate results, among others, in phenols. 2,4- and 2,6-dichlorophenols and 2,4,6-trichlorophenol were found in the pyrolyzate of Araldit in the presence of Cu(II) chloride. Only 2,4,6-trichlorophenol was obtained from a polycarbonate under similar pyrolysis conditions. The corresponding 500 °C pyrograms are shown in Fig. 10. The difference in the extent of chlorination of phenols originating from the epoxy resin on one hand and from polycarbonate on the other indicates that chlorination must occur during a transition stage of the thermal decomposition.

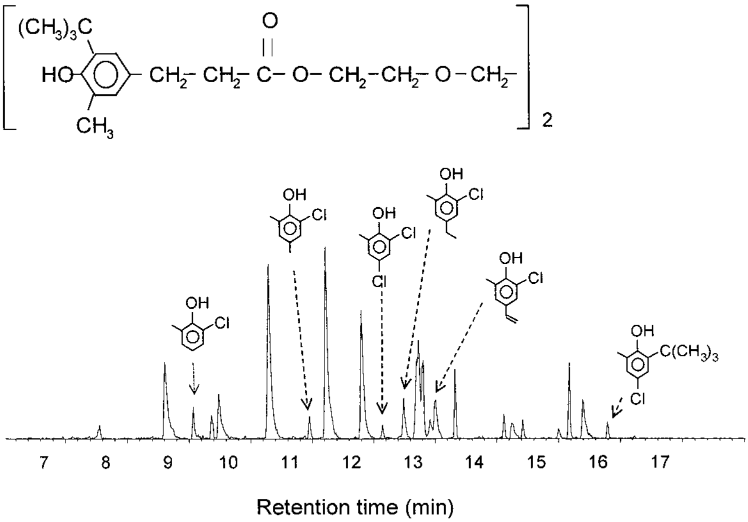

Fig. 8. Pyrogram of Irganox 245 at 700 °C in the presence of Cu(II) chloride (only chlorophenolic peaks are marked)

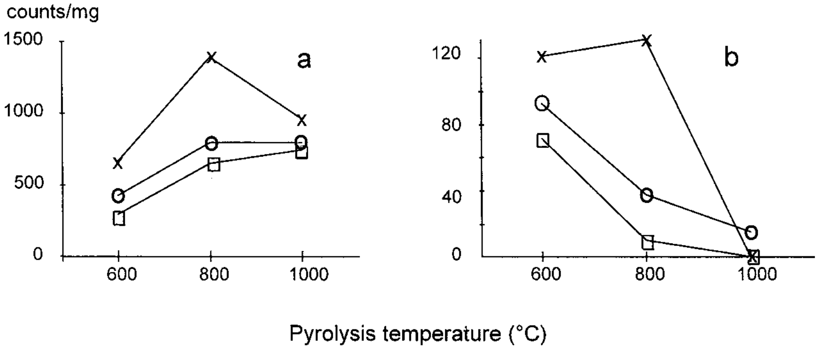

Fig. 9. Relative amounts of chlorophenolic products from pyrolysis of phenol-formaldehyde Novolak in the presence of cupric chlorides (a) and ferric chlorides (b) (X chlorophenols, □ dichlorophenols, O trichlorophenols)

EXPERIMENTAL PART

Materials

Commercial polymers and additives were used as received: poly(chlorostyrene) and poly(vinylbenzyl chloride) (60/40 mixture of 3- and 4-chloro isomers, Aldrich-Chemie); Dioxazine Violet 23 (Ciba-Geigy), and Tetrachloroisoindolinone Yellow (Microlen Yellow, Ciba-Geigy) concentrates in polyethylene, chlorinated copper phthalocyanine (Microlith Green, Bayer) concentrate in poly(vinyl chloride) - poly(vinyl acetate), Irganox 245 (Ciba-Geigy), Araldit (Ciba-Geigy AV 138 M), polycarbonate (from Bisphenol A, BDH Chemicals). Phenol-formaldehyde novolak was prepared by oxalic-acid-catalyzed condensation.

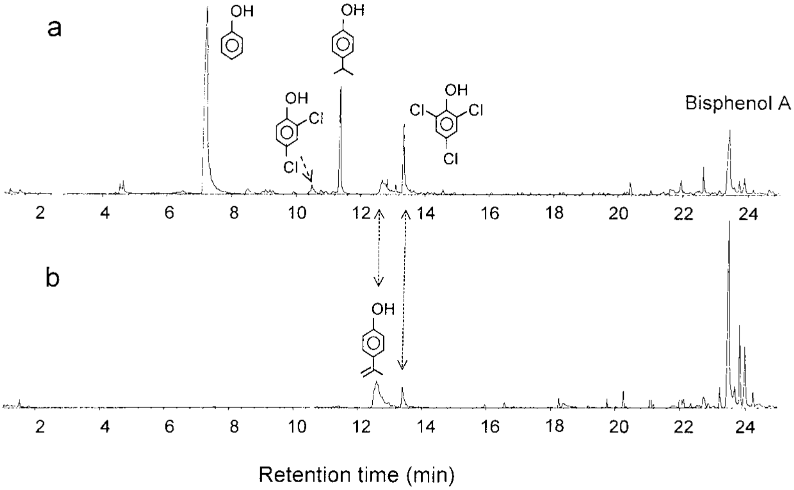

Fig. 10. Pyrolysis of Araldit (a) and polycarbonate (b) at 500 °C in the presence of cupric chloride

Pyrolysis-GC/MS

The identification of the individual compounds was based on the GC/MS analysis of fast pyrolysis products. Fast pyrolyses were performed at 500, 600, 700 or 800 °C for 20 s in a Chemical Data System Pyroprobe 120 equipped with a platinum coil and quartz sample tube interfaced to a Hewlett-Packard 5985B GC/MS. The sample mass was about 200-400 μg. A helium carrier gas of 20 ml/min flow rate purged the pyrolysis chamber held at 250°C and was split in a ratio of 1:20 before being introduced into the gas chromatograph. The GC/MS interface temperature was held at 300 °C. The mass spectrometer was operated at 70 eV in the EI mode.

Direct Probe Pyrolysis-MS

Microgram samples were heated at a rate of 30°/min from 25 to 700 °C in the direct inlet probe of a Hewlett-Packard 5985B GC/MS. The temperature was controlled by a Chemical Data System Pyroprobe 120 used in the extended mode. The mass spectrum of the evolved volatile has been scanned regularly at 15 eV in the EI mode.

CONCLUSION

Pyrolysis coupled to gas chromatography and/or mass spectrometry helped in defining some reaction pathways leading to chlorinated aromatic volatile products in thermal decomposition of plastics. Chlorinated fused aromatic compounds from poly(chlorostyrene) were formed as a consequence of the side group cleavage. Chloroaromatic products could be cleaved only from thermally unstable moieties of organic dyes. Cupric and ferric chloride proved to chlorinate phenol ester or phenol ether moieties of polymers or additives during pyrolysis.

ACKNOWLEDGEMENT

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REFERENCES

(1) G.G. Choudry, K. Olie, O. Hutzinger in: O. Hutzinger, R.W. Frei, F. Pocchiari (Eds), *Chlorinated Dioxins and Related Compounds*, Pergamon, 1982

(2) A. Blankenship, D.P.Y. Chang, A.D. Jones, P.B. Kelly, J.M. Kennedy, F. Matsumura, R. Pasek, G.S. Yang, *Chemosphere* **28**, 183 (1994)

(3) H. Kawaguchi, A. Inagaki, *Chemosphere* **28** , 57 (1994)

(4) S. Tsuge, T. Okumoto, T. Takeuchi, *Macromolecules* **2**, 200. (1969)

(5) D.L. Gardner, I.C. McNeil, *Eur. Polym. J.* **7**, 593 (1971)

(6) M. Blazsó, B.Zelei, E..Jakab, *J. Anal. Appl. Pyrolysis* **35**, 221 (1995)

(7) F. Bertini, G. Audisio, J. Kiji, *J. Anal. Appl. Pyrolysis* **33**, 213 (1995)

(8) B. Boinon, D. Ainad-Tabet, J.P. Monthard, *J. Anal. Appl. Pyrolysis* **13**, 171 (1988)

(9) G. Eklund, J.R. Pedersen, B. Stromberg, *Nature* **320**, 155 (1986)

(10) K. Ballschmitter, I. Braunmiller, R. Nemczyk, M. Swerev, *Chemosphere* **17**, 995 (1988)

(11) M. Blazsó, B. Zelei, *J. Anal. Appl. Pyrolysis* **36**, 149 (1996)

(12) W.J. Kroenke, *J. Appl. Polym. Sci.* **26**, 1167 (1981)

(13) P.Carty, E.Metcalfe, S.White, *Polymer* **33**, 2704 (1992)

(14) R. Luijk, H.A.J. Govers, G.B. Eijkel, J.J. Boon, *J. Anal. Appl. Pyrolysis* **20**, 303 (1991)

(15) M. Blazsó, *J. Anal. Appl. Pyrolysis* **40-41**, 69 (1997)