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Thermal hydrodehalogenation of 2,4-dibromophenol by polymeric materials

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Abstract

Pyrolysis appears to be an emerging option allowing recovery of useful products from wastes of electric and electronic equipment (WEEE) because of the high value of potentially accessible products such as precious metals or coke (in the residue), fuel and chemicals (pyrolysis oil and gases). However contamination of oil by harmful compounds remains a severe issue and has a strong impact on material recycling and thermal treatment: Bromine-containing phenols are classic examples of harmful compounds emitted during pyrolytic recycling of printed circuit boards, and their dehalogenation is an area of continuing scientific interest. Pyrolysis of 2,4-dibromophenol (DBP) with high density polyethylene (HDPE), low density polyethylene (LDPE), polybutadiene (PBD), polystyrene (PS), polyamide 6 (PA-6), polyamide 6,6 (PA-6,6) and polyacrylonitrile (PAN) at 290 − 370 ºC for 20 min results in the successive transformation of DBP to monobromophenols and further to phenol and HBr, together with small amounts of alkylphenols, depending on the reaction temperature and reactivity of polymers. The formation of PBDDs and PBDFs is strongly retarded despite of the structure of DBP, which favours their development. The rate of hydrodebromination decreased in the series LDPE > HDPE ≈ PBD > PS > PA-6 > PA-6,6 > PAN. The hydrodebromination process transforms the polymers studied in the highly polyaromatized char. The formation of the pyrolysis products is in favour of a radical hydrodebromination mechanism.

Introduction

About 30% in weight of the 20-50 million tons of waste yearly generated worldwide from electrical and electronic equipment (WEEE) [1] is constituted by plastics which often contains brominated flame retardants (BFR) for the most part Polybrominated diphenyl ethers and Tetrabromobisfenol A

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[2,3]. In turn Printed Circuits Boards, are mainly made of glass fibres embedded in a polymer matrix flame retarded with reactive Tetrabromobisfenol A and represent about 8% by weight of WEEE collected from small appliances [4]. There is an increasing interest in the end-of-life management of polymers present in WEEE mainly due to high quotas of recycling and recovery set by the European WEEE directives [5], which can only be fulfilled by including the plastic fraction in recycling and recovery approaches. The recycling of non metallic fraction (plastic and ceramic fractions, NMF) from waste printed circuit boards by physical and chemicals methods has been recently reviewed by Guo et al [6]: physical recycling of the NMFs is a promising method but more work should be done to develop comprehensive and industrialized usage of the recycled items; on the other hand the challenge in chemical recycling methods of the NMFs is to compensate for their higher cost of chemical recycling.

Pyrolysis appears to be an emerging option allowing recovery of useful products from WEEE because of the high value of potentially accessible products such as precious metals or coke (in the residue), fuel and chemicals (pyrolysis oil and gases). However contamination of oil by harmful compounds remains a severe issue and has a strong impact on material recycling and thermal treatment: bromine-containing phenols are classic examples of risky compounds emitted during pyrolytic recycling of polymers flame retarded with brominated fire retardants [7-10] which can form toxic polybromodibenzodioxins, PBDD, and polybromodibenzofurans, PBDF, when oil is used as a fuel. [11].

Dehalogenation of pyrolysis oil is therefore an area of continuing scientific interest. Attemps by using a tube reactor [12], copyrolysis in the presence of polyolefins [13], depolymerisation in supercritical water [14] or methanol [15], in situ treatments with CaO [16] or various catalysts [17-19] are reported. Refining of the pyrolysis oil has also be considered: hydrodehalogenation with hydrogen-donating media (tetralin, [20], conventional petroleum solvent [21], eicosane [22], 9,10-dihydroantracene [23] and PP [24]) is a promising option for the destruction of halogen-containing aromatics, which allows transformation of them to non-halogenated aromatics and hydrogen halide. In this respect PP is of advantage due to lower cost. It was found that the reaction with PP is selective and only HBr can be recovered at $290-350\ ^{\circ}C$ from a mixture of chlorinated and brominated phenols. [25].

In searching for new hydrogen-donating media it appeared important to extend the study with PP to other polymeric materials. The hydrodehalogenation of brominated phenols is believed to be radical [24], therefore reactivity of polymeric substrate towards radicals is significant. As reactivity is governed by the presence of activating (or deactivating) groups, we selected various polymer classes (polyethylenes, polybutadiene, polystyrene, polyamides and polyacrylonitrile) to hydrodebrominate a

model compound, 2,4-dibromophenol, being one of major products from pyrolysis of flame retardant polymers.

Experimental

2,4-dibromophenol (DBP) was purchased from Fluka and used as received. Polymers with different structure were used as hydrogen-donating media: high density polyethylene (HDPE), low density polyethylene (LDPE), polystyrene (PS), polyamide 6 (PA-6), polyamide 6,6 (PA-6,6) were unfilled commercial polymers supplied in pellets; polybutadiene (PBD) in form of small bales, and polyacrylonitrile (PAN) in powder were purchased from Sigma Aldrich.

To subject the polymers and their mixture with DBP to the pyrolysis PBD was cut in small pieces and, if it was the case, commercial pellets of other polymer were cut to a smaller size (about $1mm^2$). Mixture were prepared by blending the components in a ratio of about 1 mol of structural units/1 mol DBP. In some selected cases this ratio was increased to about 2. Table 1 reports composition of the mixtures.

The details of the experimental procedure have been described before [24]. Briefly explaining, pyrolysis was carried under nitrogen in encapsulated ampoules of ca. 1.7 ml at isothermal temperatures (290 - 370 °C for 20 min) to exclude volatilization of DBP. After the pyrolysis the ampoule was broken with the liberation of gaseous decomposition products and weighed. We refer to the difference of this weight and the weight of the initial ampoule as "weight of gases". Furthermore, the ampoule containing decomposition products or pyrolysis residues was washed out by dichloromethane, dried and weighed. The difference between this weight and the previous one gave the "weight of pyrolysis oil". Taking into account the initial weight of the sample and those of gases and oil, we calculated the amount of solid decomposition products (char). A part of dichloromethane-insoluble products from the pyrolysis of DBP with polyamides or PAN were soluble in water, as found by 24h extraction with water. Also in these cases the amount of water-soluble products was calculated. This method was found reproducible in the limit of 1-2 mg.

Insoluble products were characterized by FT-IR (Perkin-Elmer 2000) in KBr pellets (about 3% w/w).

The dichloromethane-soluble pyrolysis oil was analyzed using a GC/MS HP 6890/5972A. The MS detector was applied in electron impact mode. A HP-5 30 m column, temperature programmed from 40 °C (5 min) to 320 °C at a heating rate of 10 °C/min. To quantify the amount of bromine in the liquid phase we measured in the adopted GC conditions the response factor for phenol, 4-methylphenol, DBP, 2-bromophenol, 4-bromophenol, 2,4,-tribromophenol which were all found to be close to 1, therefore we considered the integrated areas % of the chromatogram representative of relative concentration of products in the pyrolysis oil; further the amount of oil (gravimetrically measured as described above) and the number of bromine per molecule were used to issue the Br balances. The limit of the sensitivity in solution was 50 ppm.

The gaseous decomposition products were analyzed by means of GC/MS. For this experiment, the 30 m HP-5 capillary column was found to be an excellent column. The column was heated to 250 °C at 10 °C per minute after initial 2 min period at −10 °C.

The decomposition products were identified by their retention time and mass spectra.

Results

Pyrolysis of DBP

Pyrolysis of DBP at 310 – 370 °C yielded gaseous product (HBr) and oil fraction. In addition, at 370 °C, the formation of a dichloromethane-not soluble product was notice, which was however liquid at the pyrolysis temperature (i.e. noncrosslinked one). As the temperature was increased the yield of HBr increased at the expenses of oil fraction (Table 2, entry 1-5). The bromine was mainly confined in the oil fraction which consisted of undecomposed DBP (85-48% decreasing with temperature from 290 to 370 °C, table 3 entries 1-5), various bromine-containing phenols and phenoxyphenols. Furthermore, the formation of brominated dibenzo-*p*-dioxins was observed at 330 °C and more consistently at 350 and 370 °C (Table 3 and Figure 1).

Pyrolysis of polymers

Thermal degradation of polymers was widely reviewed in literature [26-29]. Briefly, we expected an hydrocarbon mixture from HDPE and LDPE, monomer and oligomers from PS and PBD, cyclopentanone and nitriles from PA-6,6, caprolactame from PA-6 whereas PAN undergoes

intramolecular cyclization and progressive aromatization/charring with evolution of hydrogen, HCN and NH_3; NH_3 and CO_2 are also evolved from polyamides degradation at rather higher temperature. Considering the characteristic temperatures (melting point, mp and glass transition temperature, T_g) of the present polymers (LDPE: mp 120°C, Tg -100°C; HDPE: mp 140°C, Tg-100°C; PA-6: mp 250 °C, Tg 50°C; PA-6,6: 215°C, Tg 50°C; the not crystalline PBD, PAN PS,: Tg -100°C, 160°C and 100°C respectively) in the adopted pyrolysis conditions we expected all them be liquid state nearly as soon as the pyrolysis started.

We found that PBD, HDPE and LDPE showed no weight loss in the investigated temperature region. PAN yielded 5 % gaseous products at 310 °C and residence time 20 min. PS was dichloromethane-soluble after heating at 350 °C. Pyrolysis of PA-6 at 370 °C liberated oil fraction with a yield of 11%, whereas pyrolysis of PA-6,6 released gases and a small oil fraction (11 and 4% yield correspondently). (Table 1, entries 6-12).

Pyrolysis of DBP with PAN, PA-6, PA-6,6

Pyrolysis of DBP with PAN, PA-6, PA-6,6 resulted in the formation of oil, gaseous and water-soluble solid products, and solid residue. The yield of each fraction is reported in Table 1 entries 31-40. In addition to HBr, the pyrolysis with polyamides yielded CO_2 and a mixture of various hydrocarbons in the gases (Figures 2c and 2d). An FT-IR study was undertaken to elucidate the composition of the solid residues: the IR spectra of the pyrolyzed samples of DBP with PAN or PA-6,6 or PA-6 washed by dichloromethane exhibit strong absorption bands around 1400 and 3120 cm^{-1} which disappear in the spectra after extraction with water (Figure 3, spectra b). These bands are associated with ammonium bromide which resulted from reaction of HBr with ammonia [30]. Ammonia is therefore a pyrolysis product in addition to those reported here above: 84-100%of the organic N content is converted to water-soluble NH_4Br at 350/370 °C in the polyamides, and 79% at 330 °C in PAN (Table 2).

The yield of HBr and of the water-soluble fraction from DBP and PAN levelled-off at 330 °C. Both polyamides produced higher yield of the gaseous and water-soluble products compared to those produced by DBP and PAN. Increasing of the polyamides loading resulted in the lower formation of gases and in the higher one of water-soluble products. (Table 1).

In the presence of these polymers conversion of DBP increases (10-0% of undecomposed DBP left in the oil, Table 3): besides HBr and NH_4Br the bromine removed from DBP is confined in the unsoluble residue. Pyrolysis oil from consisted of phenol and bromine-containing phenols (Figures 6,7, 8). No PBDDs

formation was noticed beyond our detection limit. By comparing the amount of residual bromine in oils (Table 2) and their composition (table 3, and Figure 4) PA-6 was a more effective hydrodehalogenating agent than PAN and in its turn, PAN was less active than PA-6,6. Increasing of the residence time causes the bromine in oil to be converted in bromine-containing not soluble residue (table 2 and 3, entries 32 and 33)

It is important to note DBP changed pyrolysis pathways of the polymers. This was inferred comparing the FT-IR spectra of the polymers heated in the absence and presence of DBP. The main spectral changes caused by DBP are associated with development of polyaromatic absorption bands around 1590, 800 and 750 cm^{-1} (Figure 3 spectra b and c) [31-32] indicating intensive charring processes, whereas neat polyamides keep their main absorption bands during heating(Figure 3 spectra a). At 350 °C neat PAN partially keeps the nitrile band at 2240 cm^{-1} transforming to polycyclic structures [33]. Additional evidence of the influence by DBP comes from GC/MS study of pyrolysis oils. Neat PA-6 yields caprolactam during heating (Figure 4), whereas its mixture with DBP does not.

Pyrolysis of DBP with PS, PBD, LDPE and HDPE

Pyrolysis of DBP with PS, PBD, LDPE and HDPE yielded gases, oil and non soluble residue.

Gasification of DBP with PS leveled-off at 350 °C (Table entries 26-30). The main gaseous product was HBr with admixture of methyl bromide (Figure 2b). However, GC/MS analysis revealed undecomposed DBP and monobromophenols in the oil fraction (Figure 5). The peaks of bromine-contained phenols strongly decreased at 350-370°C °C due to their conversion to phenol (Fig. 5 and Table 3). Comparison of the gas chromatograms of the pyrolysis oil from neat PS and from PS + DBP showed that, in the presence of DBP, the preferential formation of alkyl benzenes, a naphthalene derivative and a terphenyl instead of styrene and its dimer and trimer which come from decomposition of polystyrene. The formation of alkylbenzenes indicates reductive medium inside of the ampoules, which is likely to come from polyaromatization of solid decomposition products, a solid residue (char) was formed indeed. However, increasing in the PS content mainly resulted in the formation of dichloromethane-soluble fraction (Table 1 entries 27-28). FT-IR analysis of the solid residue revealed the disappearance of the profile of the C-H stretch spectral region, concurrent with the broadening of the absorption band at 1594 cm^{-1} due to the formation of polyaromatic structures in the residue of the mixtures (Figure 6). The

strongest absorption bands at 752 and 698 cm^{-1} are due a monosubstituted aromatic ring. A peak at 1219 cm^{-1} is likely to be due to phenol incorporated in the char.

The amount Br in the pyrolysis oil at 330 °C for PDB and PS containing mixtures reveals that the debromuration is less effective for PS mixtures (table 2 entries 25 and 26);

PBD reacts with DBP starting from 290 °C (Table 1, entries 22-25) producing HBr together with admixture of methyl and ethyl bromides (Figure 2a). At 270 °C, only swelling of PBD with DBP was observed. The products of the hydrodebromination reaction at 290 and 310 °C are phenol and monobrominated phenols (Table 3 and Figure 5). At 330 °C pyrolysis oil was still contaminated with small amounts of monobrominated phenols and undecomposed DBP. The formation of bromine-containing phenoxyphenols and tribromodibenzodioxin was inhibited.

As shown in Table 1, gasification of DBP with polyethylenes started at 310 °C yielding the highest amount of gases among the polymers in the studied temperature interval.

In the pyrolysis oil the main product of a HDPE and DBP mixture at 310 °C was phenol (Figure 5). Increasing of temperature to 330 and 350 °C prevents the formation of brominated phenoxyphenols (Figure 5 and Table 3 entries 13-16); some amount of monobrominated phenols remained undecomposed.

The effect of LDPE on the composition of DBP pyrolysis oil is shown in Figure 5 and Table 3, entries 17-21). LDPE does not influence very much the formation of the pyrolysis products of DBP at 290 °C, whereas at 310 °C, dramatic changes were observed, as phenol admixed with monobrominated phenols was formed. At 330 and 350 °C "clean" oil was obtained in contrast to that of HDPE + DBP.

The FT-IR spectra of PBD, HDPE and LDPE treated with DBP (Figure 6) shows similar features. The CH$_2$ stretching bands and the CH$_2$ deformation band decreased in intensity. New bands around 1590 and 810 cm^{-1} formed, indicative of polyaromatic structures [31-32]. In addition, the PBD sample showed decrease in the intensity of the 1639, 966 and 727 cm^{-1} bands associated with the –CH=CH– group (Figure 14). An absorption band around 1210 cm^{-1} is likely to be due to phenol incorporated in the char.

In conclusion, HDPE appeared to be less effective than LDPE and approximately as effective as PBD. PS was less effective among C,H-polymers studied.

Discussion

The pyrolysis reactions performance was aimed at the investigation of the effects of the polymer structure and reaction temperature on the efficiency of destruction of DBP. Previous studies of dibromophenols with PP revealed optimal conditions of 350 °C in 2.0 ml ampoules [24] and of 330 °C in 1.7 ml ampoules [25] with a residence time of 20 min, indicating the impact of the reaction pressure.

The result of the study show that the pyrolysis in the presence of polymers results in the successive transformation of DBP to monobromophenols and further to phenol and HBr, together with small amounts of alkylphenols, depending on the reaction temperature and reactivity of polymers. The formation of oxygenated products such as phenoxy-phenols, PBDDs and PBDFs and of tribromo phenol is strongly retarded despite of the structure of DBP, which favour their development through coupling reactions [25]. The hydrogen bromide formed can be separated from the gas phase, whereas phenol and pyrolyzed polymers can be potentially used as fuel for combustion.

The thermal stability of brominated phenols is much lower than that of, for example, brominated diphenyl ethers and results in the formation of– bromine and less brominated phenoxyl (II) free radicals (Figure 7, reaction A) at relatively low temperature. The reason for that is believed to be phenol-keto-tautomerization which produces thermally less stable cyclohexadienone structure (I). [23, 25]. Therefore introduction of DBP in mixture with polymers eventually results in "injection" of radicals in the system before extensive degradation of polymers occurs. If appropriate hydrogen are available nearby the next step is its abstraction by the bromine/ phenoxyl radicals leading to the formation of HBr and a monobrominated phenol which again is capable of dissociation to bromine and nonbrominated phenoxyl radicals. The dissociation followed by hydrogen abstraction guarantees the complete conversion of DBP to phenol and HBr (i.e. hydrodebromination).

The present results demonstrate the effect of the hydrogen-donating media on the hydrodebromination reaction as for each particular media there is an optimal temperature range in which the reaction starts and completes within a reasonable period of time. With increasing this temperature, decreasing the hydrodebromination efficiency of the polymers is affirmed in the series (the data on PP were taken from [25]):

$$PP \approx LDPE > HDPE > PBD > PS \approx PA\text{-}6 > PA\text{-}6,6 > PAN$$
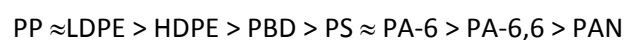
In other words, this series shows decreasing reactivity of polymers, which, in first approximation, is restricted to that of aliphatic moieties in the macromolecular chain. This approximation is especially

suited for radicals of low reactivity, such as bromine [34]. Taking into account energy considerations, the reactivity of phenoxyl radical approximates that of bromine as the gas-phase bond dissociation energy ($\Delta H_{298\ ^\circ C}$) of O-H in phenol (362.8 kJ/mol [35]) is something like that of H-Br (366.1 kJ/mol [36]). Thus, with selective radicals like bromine or phenoxyl, some positions on a molecule lose hydrogen more easily than others [34], usually with a lower C-H bond dissociation energy. These can be estimated in the polymers by comparing it to model systems from [37] and reported in table 4: The $\Delta H_{298\ ^\circ C}$ values well give an insight into why HDPE is less reactive than PP and LDPE (as containing considerably more chain branching than HDPE), however suggests that activity is not simply related to the C-H bond dissociation energies in the polymer chain indicating that other factors have to be considered indeed. For example, by treatment with radicals, alkenes are prone to undergo addition rather than substitution [34]. This will cause crosslinking of PBD (observed by swelling) and reduce its reactivity. Many anomalies were reported for alkyl side chains of aromatic rings [34], which show that the benzylic position is not always the most favored. This may be responsible for lower reactivity of PS. In addition, steric hindrance, which makes the H abstraction in the viscous polymer even more difficult to occur, should be invoked to explain the lower hydrodebromination rate of PS.

PAN is likely to undergo addition reactions with radicals to some extend. However, the main reason for deactivation hydrogens on carbon atoms next to electron-withdrawing groups , such as nitrile groups, is electrophilic character of bromine [34] which implies that it looks for positions of high electron density. Consequently, with respect to polyamides, the position α to carbonyl is deactivated. The behavior of hydrogens from a carbon adjacent to the C-N bond is not clear enough, however their abstraction is influenced by stereoelectronic effects [34]. Anyway, polyamides, are subjected to hydrolysis that leads to the formation of ammonia and less reactive hydrocarbons. In effect, compared to PE, polyamides and even more PAN are less active in a radical process such as oxidation by oxygen. This is referred to the absence of labile hydrogens in the macromolecule [33].

Other factors increasing reactivity of aliphatic polymers may be polymer radicals. At the temperature of the experiments polymer radicals resulting from hydrogen abstraction are able to produce further radicals by chain scission. Thus, primary radicals are mainly formed in HDPE; secondary radicals in PP and at the branching point of LDPE (Figure 7, reaction B). These radicals should play a role in propagating hydrodebromination reaction. Drews [38] showed that the decomposition of decabromodephenyl oxide (DBDPE) in DBDPE-PP and DBDPE-PE systems at 390 °C is assisted by radicals resulting from thermal decomposition of PP and PE. In particular, the primary radical $-CH_2^\circ$ is the most

active and is likely to attack the bromine atom of DBDPE, producing an alkyl bromide and less brominated phenyl radical that, in its turn,yields less brominated diphenyl ether due to hydrogen abstraction.

With the exception of PAN, neither of the polymers formed char in the temperature region studied (290 - 370 °C). However, an intensive formation of the char was observed in the coarse of hydrodebromination indicating that hydrogen abstraction reactions result in conversion of the polymeric backbone to polyaromatic char, which is likely to proceed through development of the conjugated double bonds, their cyclization, aromatization, fusion of aromatic rings, followed by turbostatic char formation and graphitization. The aromatization of cyclic structures gives additional hydrogen which may further help with the dehalogenation of brominated phenols.

Conclusions

The pyrolysis of 2,4-dibromophenol with the studied polymers results in the occurrence of the hydrodebromination reaction. The thermal decomposition behavior of the polymers is affected as well. The reactivity of the polymers depends on their structure: the most active is LDPE, and introducing functional groups reduces the reactivity of aliphatic hydrogens.

References

1. S. Herat, Environmental impacts and use of brominated flame retardants in electrical and electronic equipment, Environmentalist 28 (2008) 348–357

2. M. Alaee, P. Arias, A. Sjödin, Å. Bergman, An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release, Environ. Int. 29 (6) (2003) 683-689

3. M. Schlummer, L. Gruber, A. Mäurer, G. Wolz, R. van Eldik, Characterisation of polymer fractions from waste electrical and electronic equipment (WEEE) and implications for waste management, Chemosphere 67 (2007) 1866–1876

4. WRAP Waste & Resources Action Programme Project MDD009 'Compositional analysis of kerbside collected small WEEE' Final Report, February 2009]

5. Directive 2002/96/EC of the European Parliament and of the Council of 27 January 2003 on waste electrical and electronic equipment (WEEE); Directive 2003/108/EC of the European Parliament and of the Council of 8 December 2003 amending Directive 2002/96/EC on waste electrical and electronic equipment (WEEE); Directive 2008/34/EC of the European Parliament and of the Council of 11 March 2008 amending Directive 2002/96/EC on waste electrical and electronic equipment (WEEE),

6. J. Guo, Z. Xu, recycling of non metallic fractions from waste printed circuit boards: a review, J. Hazard Mater. 168 (2009) 567-590

7. M.P. Luda, N. Euringer, U. Moratti, M. Zanetti, WEEE recycling: Pyrolysis of fire retardant model polymers, Waste Manage. 25 (2005) 203–208

8. F. Barontini, V. Cozzani, Formation of hydrogen bromide and organobrominated compounds in the thermal degradation of electronic boards, J. Anal. Appl. Pyr. 77 (2006) 41–55

9. M. Blazsó, Z. Czégény, C. Csoma, Pyrolysis and debromination of flame retarded polymers of electronic scrap studied by analytical pyrolysis, J. Anal. Appl. Pyr. 64 (2) (2002) 249-261

10. G. Grause, M. Furusawa, A. Okuwaki, T. Yoshioka. Pyrolysis of Tetrabromobisphenol-A containing laminated printed circuit boards, Chemosphere 71 (2008) 872-878

11. R. Weber, B. Kuch, Relevance of BFRs and thermal conditions on the formation pathways of brominated and brominated–chlorinated dibenzodioxins and dibenzofurans. .Environ. Int. 29 (2003) 699–710.

12. N. Miskolczi, W.J. Hall , A. Angyal, L. Bartha, P.T. Williams, Production of oil with low organobromine content from the pyrolysis of flame retarded HIPS and ABS plastics, J. Anal. Appl. Pyrolysis 83 (2008) 115–123

13. W.J. Hall a, N. Merry, M. Mitan , T. Bhaskar, A. Muto, Y. Sakata, P. T. Williams, The co-pyrolysis of flame retarded high impact polystyrene and polyolefins J. Anal. Appl. Pyrolysis 80 (2007) 406–415

14. J. A. Onwudili, P. T.Williams Degradation of brominated flame-retarded plastics (Br-ABS and Br-HIPS) in supercritical water, J. of Supercritical Fluids 49 (2009) 356–368

15. Xiu Fu-Rong, Zang Fu-Shen, Materials recovery from waste printed circuit boards by supercritical methanol, J. Hazard. Mater. 178 (2010) 628–634

16. Yi - Chieh Lai , Wen - Jhy Lee, Hing – Wang Ly, Inhibition of Polybrominated Dibenzo-p-dioxin and Dibenzofuran Formation from the Pyrolysis of Printed Circuit Boards, Environ. Sci. Technol. 41 (2007) 957-962

17. W. J. Hall, N. Miskolczi, J. Onwudili, P. T. Williams, Thermal Processing of Toxic Flame-Retarded Polymers Using a Waste Fluidized Catalytic Cracker (FCC) Catalyst Energy & Fuels, 22 (2008) 1691–1697;

18. C. Vasile, M. A. Brebu, T. Karayildirim, J. Yanik, H. Darie, Feedstock recycling from plastics and thermosets fractions of used computers. II. Pyrolysis oil upgrading, Fuel 86 (2007) 477–485

19. W.J. Hall, P. T. Williams, Removal of organobromine compounds from the pyrolysis oils of flame retarded plastics using zeolite catalysts J. Anal. Appl. Pyrolysis 81 (2008) 139–147

20. Y. Sato, Y. Kodera, T. Kamo, Effect of Solvents on the Liquid-Phase Cracking of Thermosetting Resins, Energy& Fuel, 13 (2) (1999), 364-368.

21. T. Kamo, Y.Kondo, K. Pondera, S. Kushiyama,Proceeding of the 2nd IFSR Oostende (2002)

22. E.J.C. Borojovich, Z. Aizenshtat, Thermal behavior of brominated and polybrominated compounds I: closed vessel conditions, J. Anal. Appl. Pyr., 63 (2002) 129-145.

23. P. Mulder, I.W.C.E. Arends, D. Santoro; H. G. Korth, The surprisingly facile thermal dehalogenation of chlorinated aromatics by a hydroaromatic donor solvent. Tautomerization of chlorinated phenols and anilines, J. Org. Chem. 68 (2003) 4247-4257.

24. A. Hornung, A.I.Balabanovich, S. Donner, H., Seifert, Detoxification of brominated pyrolysis oils, J. Anal. Appl. Pyr. 70 (2003) 723-733.

25. A.I. Balabanovich, A. Hornung, M.P. Luda, W. Koch , V. Tumiatti, Pyrolysis study of halogen-containing aromatics reflecting reactions with PP in a post-treatment decontamination process, Env. Sci Tech. 39(14) (2005) 5469-5474

26. N. Grassie, G. Scott, Polymer Degradation and Stabilization, Cambridge University Press 1985

27. S.V. Levchik, E.D. Weil, M. Lewin, Thermal decomposition of aliphatic nylons, Polym. Intern. 48 (6-7) (1999) 532-557

28. N. H. Huang, J. Q. Wang, Investigation on the thermal degradation of polyamide 6 by thermogravimetric analysis coupled to Fourier transform infrared spectroscopy, Beijing Ligong Daxue Xuebao/Transaction of Beijing Institute of Technology 24 (2) (2004), 182-184

29. M. A.Schaffer, E. K. Marchildon, K. B. Mcauley, M. F. Cunningham, Thermal Nonoxidative Degradation of Nylon 6,6, Polym. Rev. 40 (4) (2000) 233-272

30. G. Socrates, Infrared and Raman Characteristic group frequencies. Tables and Charts, Third Edition, John Wiley&Sons, Chichester, 2004

31. Morterra, C.; Low, M.J.D. An Infrared Spectroscopic Study of some Carbonaceous Materials, Mater. Chem. Phys. 12(3) (1985) 207-233

32. L. Costa, M. Avantaneo, P.Bracco, V. Brunella Char formation in polyvinyl polymers I. Polyvinyl acetate, Polym. Degr. Stab. 77 (2002) 503-510

33. N. Grassie, Pyrolysis of Acrylonitrile Homopolymers and Copolymers, Dev in Polym. Degr. 1 (1977) 137-169

34. M.B. Smith, J. March, March's advanced organic chemistry: reactions, mechanisms, and structure", 5th edition, John Wiley, New York, 2001.

35. P. Mulder, H.G. D.Korth, A. Pratt, G.A. diLabio, L. Valgimigli, G.F.Pedull, K.U. Ingold, Critical re-evaluation of the O-H bond dissociation enthalpy in phenol, J. Phys. Chem. A 109 (2005) 2647-2655

36. S. J. Blanksby,; G. B. Ellison, Bond dissociation energies of organic molecole, Acc. Chem. Res. 36 (2003) 255-263

37. CRC Hanbook of Chemistry and Physics, 80th ed, Ed D.R. Lide, 1999 New York, CRC Press 9-64- 9-65

38. M. J. Drews, C.W. Jarvis, G. Lickfield, Ternary Reactions among Polymer Substrates, Organohalogens and Metal Oxide in condensed Phase under pyrolytic Conditions, in G.L Nelson (Ed) Fire and Polymer Hazards Identification and Prevention; ACS Symposium series n 425 (1990) 109-129

Caption to the figures

Figure 1. Total ion gas chromatogram of the pyrolysis oil of DBP from: 290 °C for 20 min (a), 330 °C for 20 min (b), 370 °C for 20 min (c). 1 – 2-bromophenol, 2 – 4-bromophenol, 3 – 2,4-dibromophenol, 4 – 2,6-dibromophenol, 5 – 1,3,5-tribromobenzene, 6 – 2,4,6-tribromophenol, 7 – 2-(2,4-dibromophenoxy)phenol, 8 – dibromodibenzodioxin, 9 – tribromophenoxyphenol, 10 – tribromodibenzodioxin, 11 - tetrabromophenoxyphenol.

Figure 2. Total ion gas chromatogram of the gaseous products of: DBP + PBD = 73 + 18 (mg) from 310 °C for 20 min (a), DBP + PS = 74 + 38 (mg) from 370 °C for 20 min (b), DBP + PA-6 = 73 + 28 (mg) from 370 °C for 20 min (c), DBP + PA-6,6 = 76 + 22 (mg) from 370 °C for 20 min (d). 1 – air, 2 – air + CO2, 3 – HBr, 4 – acetone, 5 – methyl bromide, 6 – 2-methylbutane, 7 – pentane, 8 – ethyl bromide, 9 – 2-methylpentane, 10 – hexane, 11 – benzene.

Figure 3. Pyrolysis of nitrogen-containing polymers and their mixtures with DBP: FT-IR spectra of solid products (residue) from: neat polymer (a); Polymer+ DBP (b); Polymer + DBP after extraction with water. (c)

Figure 4. Total ion gas chromatogram of the pyrolysis oils of nitrogen-containing polymers and their mixtures with DBP. . (brominated are underlined)

1 – phenol, 2 – 2-bromophenol, 3 – 4-bromophenol, 4 – 2,4-dibromophenol, 5 – 2,6-dibromophenol, 6 – 2,4,6-tribromophenol, 7 – tribromophenoxyphenol, 8 – 2-methylphenol, , 9 – 4-methylphenol 10 – dibenzofuran, 11 – caprolactam,12 – 4-ethylphenol, 13 – 4-(1,1-dimethylethyl)phenol,

Figure 5. Total ion gas chromatogram of the pyrolysis oil of hydrocarbon polymers and their mixtures with DBP. (brominated are underlined)

 1 – phenol, 2 – 2-bromophenol, 3 – 4-bromophenol, 4 – 2,4-dibromophenol, 5 – dibenzofuran, 6 – 2-phenoxyphenol, 7 – 2,4,6-tribromophenol, 8 – 4-phenoxyphenol, 9 – 4-(2,4-dibromophenoxy)phenol, 10 – tribromophenoxyphenol, 11 – 2-(2,4-dibromophenoxy)phenol, 12 – 2,6-dibromophenol, 13 – styrene, 14 – 1,1'-(1,3-propanediyl)bisbenzene, 15 – styrene dimer, 16 – 1-phenylnaphthalene, 17 – styrene trimer, 18 – 5'-phenyl-1,1':3'1''-terphenyl. 19 – toluene, 20 – ethylbenzene, 21 – isopropylbenzene,

Figure 6. Pyrolysis of hydrocarbon polymers and their mixtures with DBP: FT-IR spectra of the residues of neat polymer (a) of polymer + DBP after extraction with dichloromethane.

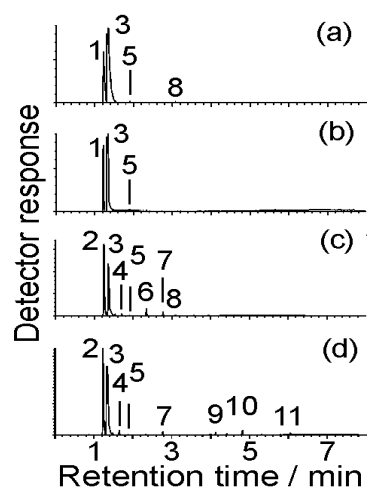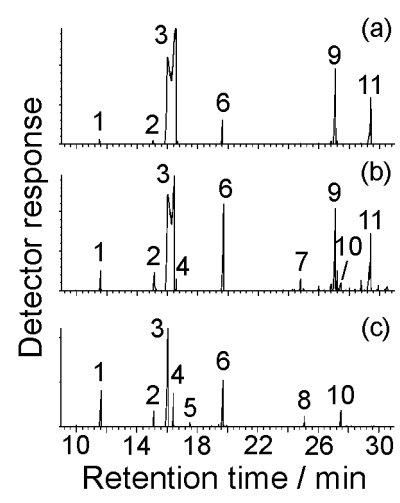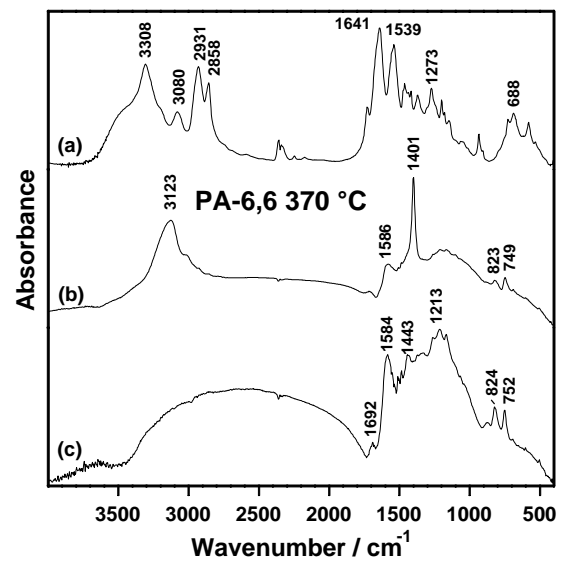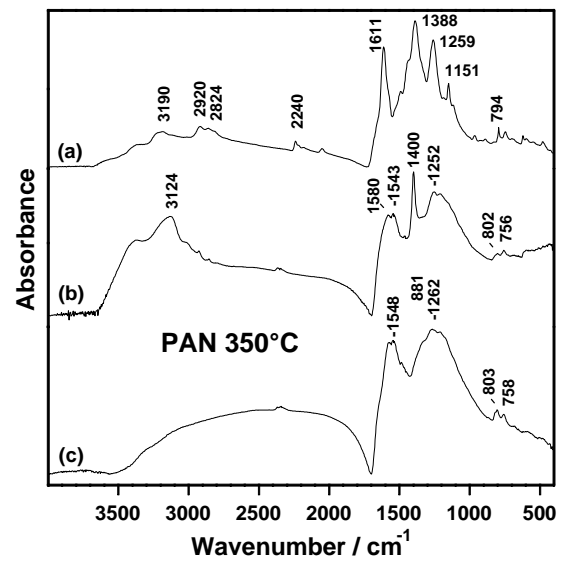Figure 7 Formation of radicals from pyrolysis of the systems under study.

Fig 1

Fig. 2

PAN 350°C

(a) 3190, 2920, 2824, 2240, 1611, 1388, 1259, 1151, 794
(b) 3124, 1580, 1543, 1400, 1252, 802, 756
(c) 1548, 881, 1262, 803, 758

PA-6,6 370 °C

(a) 3308, 3080, 2931, 2858, 1641, 1539, 1273, 688
(b) 3123, 1586, 1401, 823, 749
(c) 1692, 1584, 1443, 1213, 824, 752

Fig. 3

Detector response

(a)

2

1

3 4 4 5

6

7

DBP + PAN   310 °C

(b)

2

1

3

4 5

6

DBP + PAN   330 °C

(c)

2

1

3 4

4

5

6

DBP + PAN   350 °C

Retention time / min

10   14   18   22   26   30

3

9   4

2   3
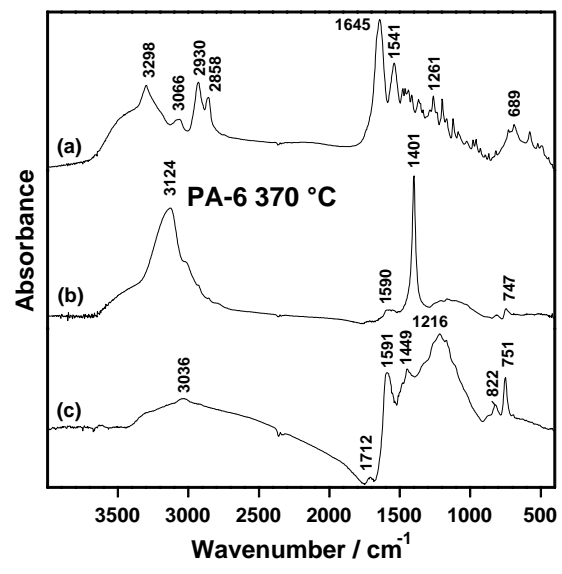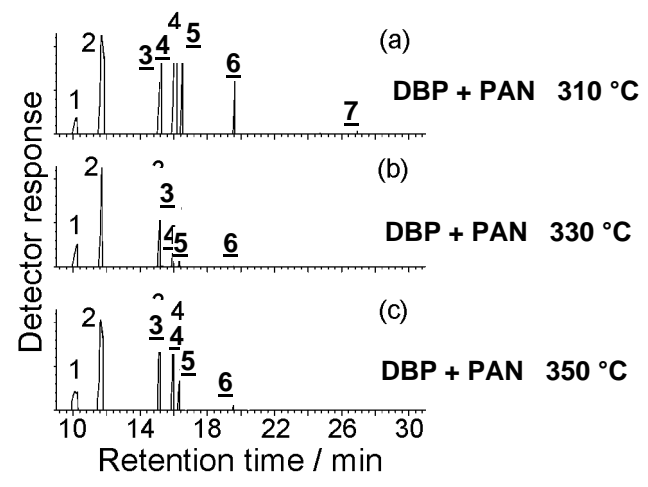
DBP + PA-6,6   350 °C

4 5

10

DBP + PA-6,6   370 °C

PA-6   370 °C

DBP + PA-6   350 °C

DBP + PA-6   370 °C
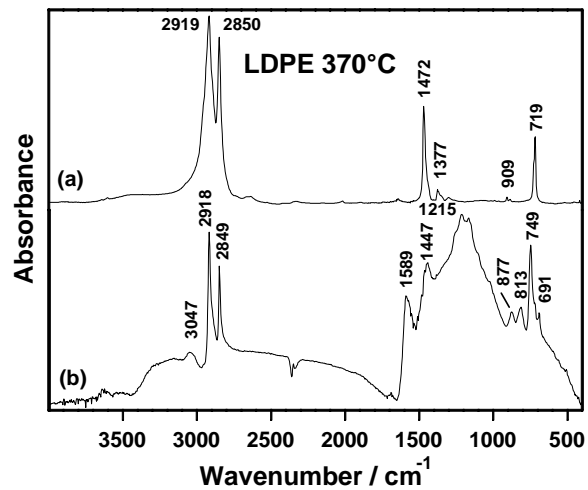
4 5

3 4

5

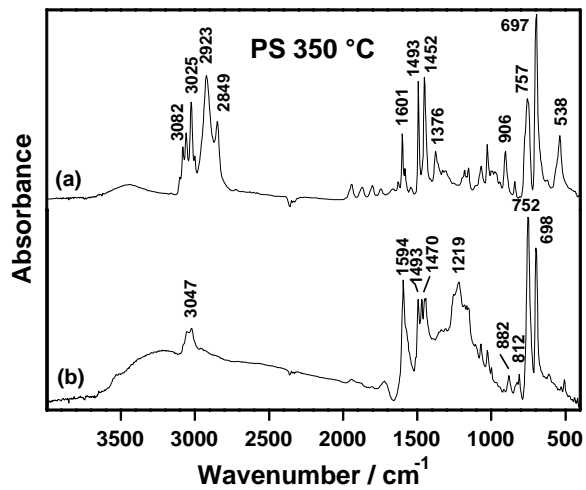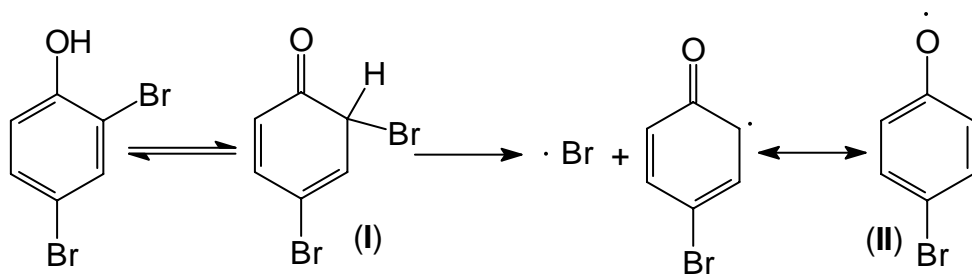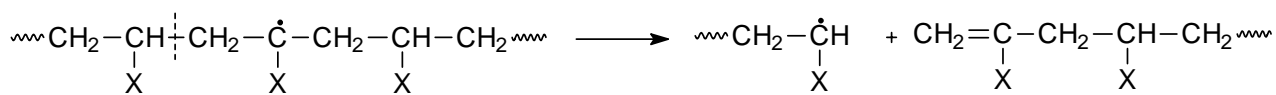6
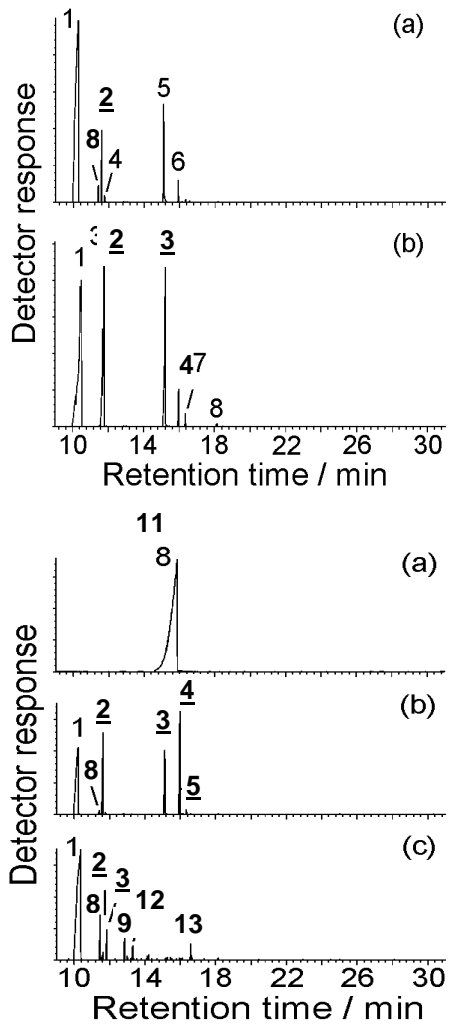
Fig.4
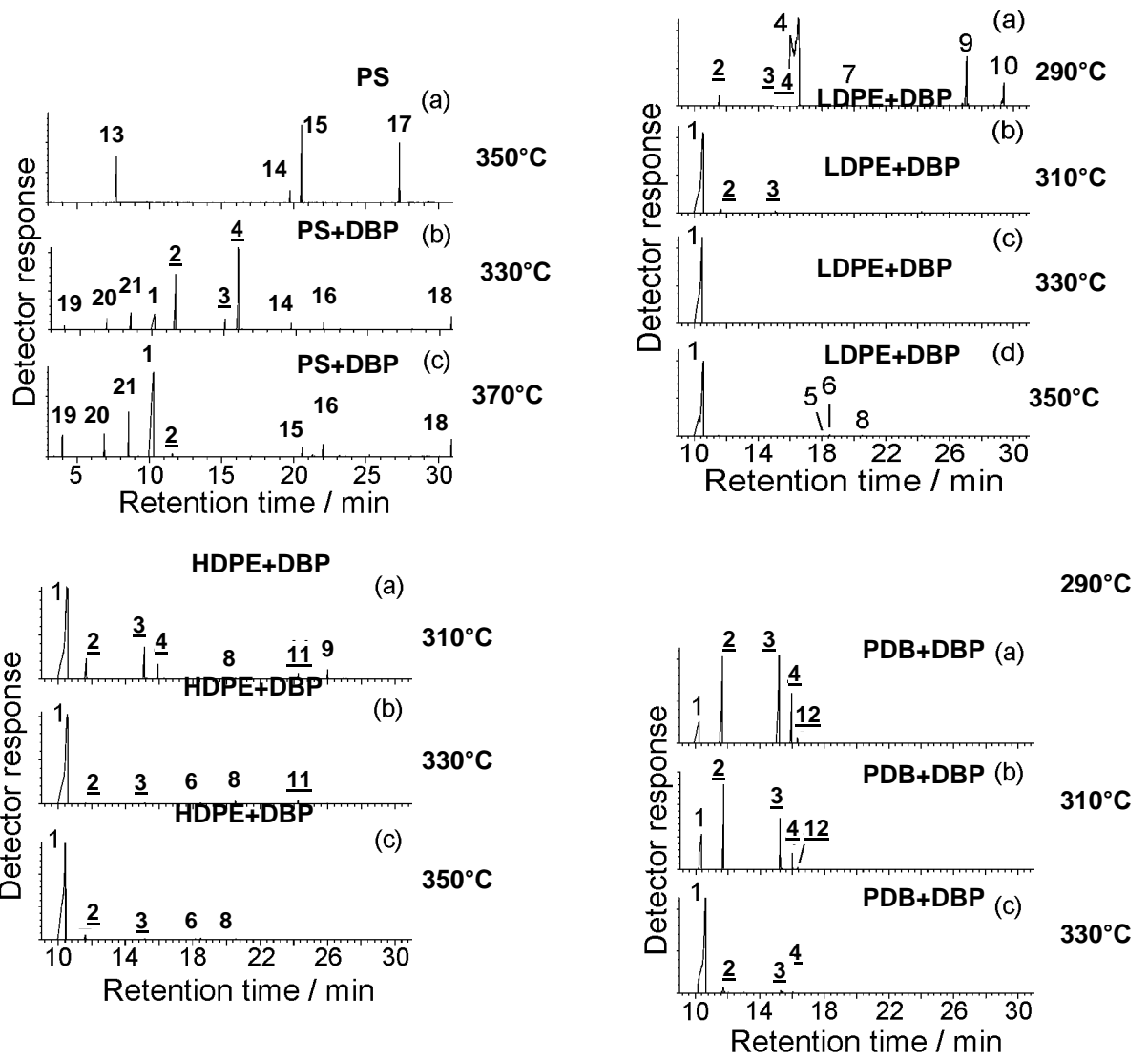
Fig.5
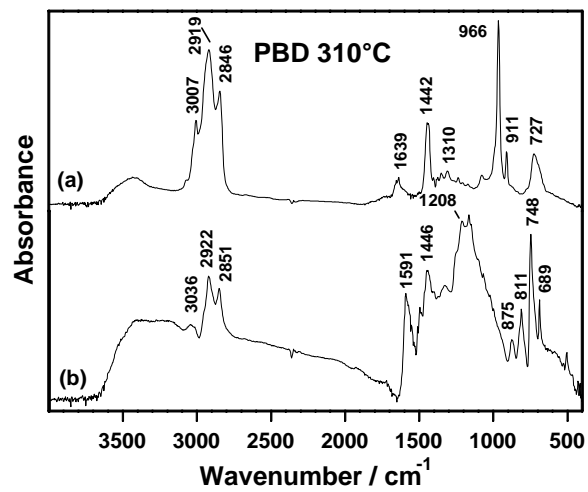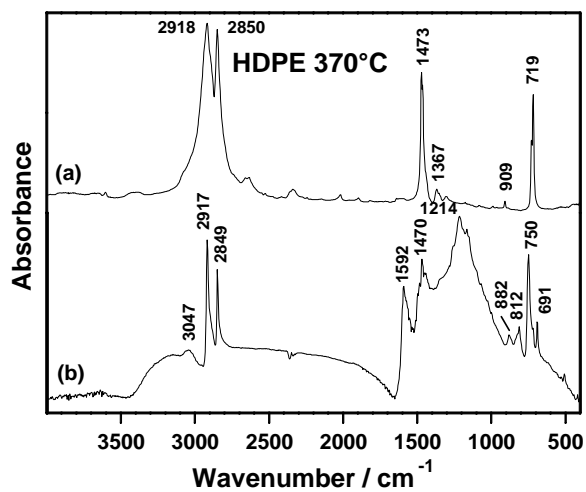
Fig.6

Reaction A

HDPE: X= H;   PP: X=CH$_3$;   PS: X= Ph;   LDPE (branching points): X= ---CH$_2$;   PAN   X=CN

Reaction B

Fig.7

Table 1, Yield of fractions from pyrolysis of 2,4-dibromophenol with polymers (encapsulated ampoules, under nitrogen)

Entry	Composition	t (°C)	time (min)	gases	oil	residue	water sol,
		Pyrolysis		Yield [a] (wt,%) of			
1	DBP (83,2 mg)	290	20	0	100	0	
2	DBP (80,3 mg)	310	20	0,6	99,4	0	
3	DBP (78,2 mg)	330	20	3	97	0	
4	DBP (77,8 mg)	350	20	7	93	0	
5	DBP (63,9 mg)	370	20	20	77	3	
6	HDPE (72,0 mg)	370	20	0	0	100	
7	LDPE (70,0 mg)	370	20	0	0	100	
8	PBD (85,2 mg)	310	20	0	0	100	
9	PS (60,9 mg)	350	20	0	100	0	
10	PAN (49,2 mg)	310	20	5	0		
11	PA-6 (76,6 mg)	370	20	0	11	89	
12	PA-6,6 (84,9 mg)	370	20	11	4	85	
13	DBP+HDPE = 71,1 + 13,8 (mg)	310	20	39	33	28	
14	DBP+HDPE = 70,1 + 12,0 (mg)	330	20	42	34	24	
15	DBP+HDPE = 76,1 + 11,9 (mg)	350	20	45	34	21	
16	DBP+HDPE = 79,1 + 12,3 (mg)	370	20	43	36	21	
17	DBP+LDPE = 74,8 + 13,8 (mg)	290	20	0	52	48	
18	DBP+LDPE = 76,9 + 13,8 (mg)	310	20	42	44	14	
19	DBP+LDPE = 78,2 + 14,2 (mg)	330	20	46	29	25	
20	DBP+LDPE = 74,7 + 13,3 (mg)	350	20	43	34	23	
21	DBP+LDPE = 79,6 + 12,2 (mg)	370	20	47	37	16	
22	DBP+PBD = 73,8 + 19,1 (mg)	270	20	0	40	60	
23	DBP+PBD = 72,8 + 19,0 (mg)	290	20	33	32	35	
24	DBP+PBD = 72,8 + 18,5 (mg)	310	20	37	31	32	
25	DBP+PBD = 78,1 + 18,3 (mg)	330	20	38	34	28	
26	DBP + PS = 73,9 + 37,5 (mg)	330	20	21	79	0	
27	DBP + PS = 73,1 + 44,8 (mg)	350	20	30,5	69	0,5	
28	DBP + PS = 74,4 + 36,8 (mg)	350	20	38	32	30	
29	DBP + PS = 73,2 + 35,7 (mg)	370	20	36	26	38	
30	DBP + PS = 73,9 + 38,5 (mg)	370	20	34	31	35	
31	DBP+PA-6 = 76,7 + 20,5 (mg)	350	20	23	36	21	20
32	DBP+PA-6 = 77,7 + 25,7 (mg)	370	20	20	32	26	22
33	DBP+PA-6 = 73,5 + 27,7 (mg)	370	26	16	35	29	20
34	DBP+PA-6 = 76,3 + 40,6 (mg)	370	20	10	38	27	25
35	DBP+PA-6,6 = 75,7 + 19,5 (mg)	350	20	30	31	23	16
36	DBP+PA-6,6 = 76,3 + 21,9 (mg)	370	20	27	34	21	18
37	DBP+PA-6,6 = 74,3 + 41,3 (mg)	370	20	8	36	28	28
38	DBP+PAN = 79,5 + 18,7 (mg)	310	20	9	46,5	44	0,5
39	DBP+PAN = 72,7 + 22,6 (mg)	330	20	17	28	39	16
40	DBP+PAN = 74,6 + 24,4 (mg)	350	20	16	32	39	13

		Pyrolysis conditions				% of total Br in the pyrolysis fractions				% of total N in the pyrolysis fractions	
Entry	components	DBP mg	Polym. mg	T (°C)	Time min	gases	oil	Resi-due	H$_2$O sol.	Resi-due	H$_2$O sol.
1	DBP	83,2	0	290	20	0	99	1	0	-	-
2	DBP	80,3	0	310	20	1	97	2	0	-	-
3	DBP	78,2	0	330	20	5	88	7	0	-	-
4	DBP	77,8	0	350	20	11	89	0	0	-	-
5	DBP	63,9	0	370	20	31	69	0	0	-	-
13	DBP+HDPE	71,1	13,8	310	20	72	5	23	0	-	-
14	DBP+HDPE	70,1	12,0	330	20	77	tr	23	0	-	-
15	DBP+HDPE	76,1	11,9	350	20	81	tr	19	0	-	-
16	DBP+HDPE	79,1	12,3	370	20	77	0	22	0	-	-
17	DBP+LDPE	74,8	13,8	290	20	0	61	39	0	-	-
18	DBP+LDPE	76,9	13,8	310	20	77	1	22	0	-	-
19	DBP+LDPE	78,2	14,2	330	20	85	0	15	0	-	-
20	DBP+LDPE	74,7	13,3	350	20	79	0	21	0	-	-
21	DBP+LDPE	79,6	12,2	370	20	84	0	16	0	-	-
22	DBP+PBD	73,8	19,1	270	20	0	51	49	0	-	-
23	DBP+PBD	72,8	19,0	290	20	65	25	10	0	-	-
24	DBP+PBD	72,8	18,5	310	20	72	16	12	0	-	-
25	DBP+PBD	78,1	18,3	330	20	73	1	26	0	-	-
26	DBP + PS	73,9	37,5	330	20	49	51	0	0	-	-
27	DBP + PS	73,1	44,8	350	20	77	tr	23	0	-	-
28	DBP + PS	74,4	36,8	350	20	88	tr	11	0	-	-
29	DBP + PS	73,2	35,7	370	20	83	0	17	0	-	-

30	DBP + PS	73,9	38,5	370	20	80	0	20	0	-	-
31	DBP+PA-6	76,7	20,5	350	20	45	20	2	33	4	96
32	DBP+PA-6	77,7	25,7	370	20	35	1	26	38	0	100
33	DBP+PA-6	73,5	27,7	370	26	29	tr	35	36	14	85
34	DBP+PA-6	76,3	40,6	370	20	20	5	25	50	14	84
35	DBP+PA-6,6	75,7	19,5	350	20	59	4	12	26	9	91
35	DBP+PA-6,6	76,3	21,9	370	20	48	15	6	30	6	94
37	DBP+PA-6,6	74,3	41,3	370	20	17	14	12	57	9	91
38	DBP+PAN	79,5	18,7	310	20	17	80	3	tr	100	tr
39	DBP+PAN	72,7	22,6	330	20	35	23	15	27	21	79
40	DBP+PAN	74,6	24,4	350	20	33	30	15	22	39	61

Table 2. % of total Br and of total N in the fractions from the pyrolysis of 2,4-dibromophenol and its mixtures with polymers (encapsulated ampoules, under nitrogen)

Table 3. % of total Br in the classes of compounds found in the pyrolysis oil of 2,4-dibromophenol and its mixtures with polymers (encapsulated ampoules, under nitrogen) (tr=<0.5%)

		Pyrolysis conditions				% of total Br in the products of pyrolysis oil				
Entry	components	DBP mg	Polym. mg	T (°C)	Time min	DBP[a]	MBP[b]	TBP[c]	other[d]	POP[e]
1	DBP	83,2	0	290	20	85	tr	2	0	12
2	DBP	80,3	0	310	20	70	1	5	0	21
3	DBP	78,2	0	330	20	68	2	2	1°	15
4	DBP	77,8	0	350	20	55	5	27	3°	6
5	DBP	63,9	0	370	20	48	11	8	3°	0
13	DBP+HDPE	71,1	13,8	310	20	1	4	0	tr	tr
14	DBP+HDPE	70,1	12,0	330	20	0	tr	0	0	tr
15	DBP+HDPE	76,1	11,9	350	20	0	tr	0	0	0
16	DBP+HDPE	79,1	12,3	370	20	0	tr	0	0	0
17	DBP+LDPE	74,80	13,8	290	20	54	1	1	0	5
18	DBP+LDPE	76,90	13,8	310	20	0	1	0	tr°	0
19	DBP+LDPE	78,20	14,2	330	20	0	0	0	0	0
20	DBP+LDPE	74,70	13,3	350	20	0	0	0	0	0
21	DBP+LDPE	79,60	12,2	370	20	0	0	0	0	0
22	DBP+PBD	73,80	19,1	270	20	51	tr	0	0	0
23	DBP+PBD	72,80	19,0	290	20	5	20	0	0	0
24	DBP+PBD	72,80	18,5	310	20	1	15	0	0	0
25	DBP+PBD	78,10	18,3	330	20	tr	1	0	0	0
26	DBP + PS	73,90	37,5	330	20	37	14	0	0	0
27	DBP + PS	73,10	44,8	350	20	0	tr	0	0	0
28	DBP + PS	74,40	36,8	350	20	0	tr	0	0	0

29	DBP + PS	73,20	35,7	370	20	0	0	0	0	0
30	DBP + PS	73,90	38,5	370	20	0	0	0	0	0
31	DBP+PA-6	76,70	20,5	350	20	10	10	0	0	0
32	DBP+PA-6	77,70	25,7	370	20	0	1	0	0	0
33	DBP+PA-6	73,50	27,7	370	26	0	tr	0	0	0
34	DBP+PA-6	76,30	40,6	370	20	tr	2	0	3*	0
35	DBP+PA-6,6	75,70	19,5	350	20	1	3	0	0	0
36	DBP+PA-6,6	76,30	21,9	370	20	1	14	0	0	0
37	DBP+PA-6,6	74,30	41,3	370	20	2	10	0	2*	0
38	DBP+PAN	79,50	18,7	310	20					
39	DBP+PAN	72,70	22,6	330	20	4	19	0	0	0
40	DBP+PAN	74,60	24,4	350	20	9	21	tr	0	0

[a]DBP dibromophenols

[b]MBP mono bromophenols

[c]TBP tribromophenols

[d]other brominated (brominated hydrocarbons*, brominated dibenzodioxins°)

[e]POP brominated phenoxy phenols
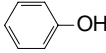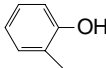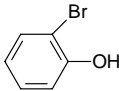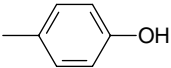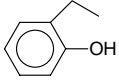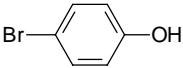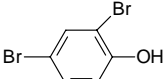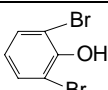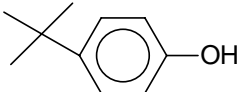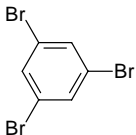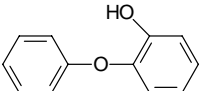
Table 4 $\Delta H_{298°C}$ for dissociation of bonds involving formation of radicals that can be formed by hydrogen abstraction by the polymers under investigation

Bond	$\Delta H^{dissociation}$ (298°C) kJ/mol	Polymers containing that bond
Allylic C-H	345	PBD
α-phenyl C-H	353	PS
α-nitrile C-H	362	PAN
α-amine C-H	364	*
tert- C-H	404	LDPE, PP
Methylene C-H	409	HDPE, LDPE, PS, PP
α-carbonyl C-H	411	PA-6, PA-6,6

*PA-6 and PA-6,6 contain an α-amide C-H

Additional information

Table 1 Main degradation products in the pyrolysis oil of DBP and of its mixtures with p+DBP (Br=79 a.m.u.)

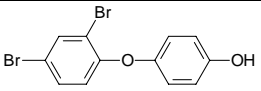| MW	Ret. Time (min)	Compounds	Molecular Structure	MS attribution; Ref.
94	10.82	Phenol		Wiley and NBS MS library
108	11.40	2-methylphenol		Wiley and NBS MS library
172	11.52	2-bromophenol		Wiley and NBS MS library
108	11.76	4-methylphenol		Wiley and NBS MS librar
122	12.81	2-ethylphenol		Wiley and NBS MS library
122	12.87	2-ethylphenol		Wiley and NBS MS library
172	15.08	4-bromophenol		Wiley and NBS MS library
250	15.97	2,4-dibromophenol		Wiley and NBS MS library
250	16.35	2,6-dibromophenol		Wiley and NBS MS library
150	16.54	4(1,1dimethyl ethyl)phenol		Wiley and NBS MS library
312	19.59	1,3,5-tribromobenzene		Wiley and NBS MS library
186	18.47	2-phenoxyphenol		Wiley and NBS MS library
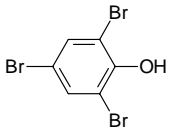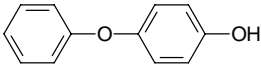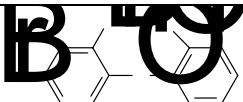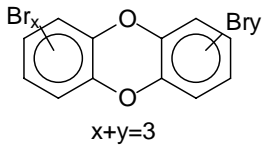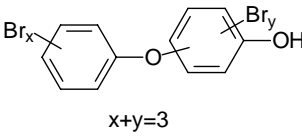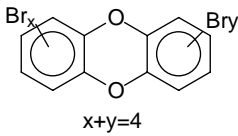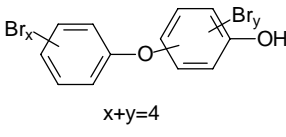
MW	Ret. Time (min)	Compounds	Molecular Structure	MS attribution; Ref.
358	19.63	1,3,5-tribromophenol		Wiley and NBS MS library
186	20.54	4-phenoxyphenol		Wiley and NBS MS library
342	24.25	2-(2,4-dibromo phenoxy)phenol		Assignation based on the MS pattern [25]
418	25.09	Dibromodibenzo dioxin	x+y=3	[24]
342	25.99	4-(2,4-dibromo phenoxy)phenol		Assignation based on the MS pattern [25]
420	27.05	Tribromo phenoxyphenol	x+y=3	[25]
340	27.49	tetrabromodibenzo dioxin	x+y=4	[24]
498	29.43	Tetrabromo phenoxyphenol	x+y=4	Assignation based on the MS pattern [25]

Table 1, Yield of fractions from pyrolysis of 2,4-dibromophenol with polymers (encapsulated ampoules, under nitrogen)

Entry	Composition	Pyrolysis		Yield [a] (wt,%) of			
		t (˚C)	time (min)	gases	oil	residue	water sol,
1	DBP (83,2 mg)	290	20	0	100	0	
2	DBP (80,3 mg)	310	20	0,6	99,4	0	
3	DBP (78,2 mg)	330	20	3	97	0	
4	DBP (77,8 mg)	350	20	7	93	0	
5	DBP (63,9 mg)	370	20	20	77	3	
6	HDPE (72,0 mg)	370	20	0	0	100	
7	LDPE (70,0 mg)	370	20	0	0	100	
8	PBD (85,2 mg)	310	20	0	0	100	
9	PS (60,9 mg)	350	20	0	100	0	
10	PAN (49,2 mg)	310	20	5	0		
11	PA-6 (76,6 mg)	370	20	0	11	89	
12	PA-6,6 (84,9 mg)	370	20	11	4	85	
13	DBP+HDPE = 71,1 + 13,8 (mg)	310	20	39	33	28	
14	DBP+HDPE = 70,1 + 12,0 (mg)	330	20	42	34	24	
15	DBP+HDPE = 76,1 + 11,9 (mg)	350	20	45	34	21	
16	DBP+HDPE = 79,1 + 12,3 (mg)	370	20	43	36	21	
17	DBP+LDPE = 74,8 + 13,8 (mg)	290	20	0	52	48	
18	DBP+LDPE = 76,9 + 13,8 (mg)	310	20	42	44	14	
19	DBP+LDPE = 78,2 + 14,2 (mg)	330	20	46	29	25	
20	DBP+LDPE = 74,7 + 13,3 (mg)	350	20	43	34	23	
21	DBP+LDPE = 79,6 + 12,2 (mg)	370	20	47	37	16	
22	DBP+PBD = 73,8 + 19,1 (mg)	270	20	0	40	60	
23	DBP+PBD = 72,8 + 19,0 (mg)	290	20	33	32	35	
24	DBP+PBD = 72,8 + 18,5 (mg)	310	20	37	31	32	
25	DBP+PBD = 78,1 + 18,3 (mg)	330	20	38	34	28	
26	DBP + PS = 73,9 + 37,5 (mg)	330	20	21	79	0	
27	DBP + PS = 73,1 + 44,8 (mg)	350	20	30,5	69	0,5	
28	DBP + PS = 74,4 + 36,8 (mg)	350	20	38	32	30	
29	DBP + PS = 73,2 + 35,7 (mg)	370	20	36	26	38	
30	DBP + PS = 73,9 + 38,5 (mg)	370	20	34	31	35	
31	DBP+PA-6 = 76,7 + 20,5 (mg)	350	20	23	36	21	20
32	DBP+PA-6 = 77,7 + 25,7 (mg)	370	20	20	32	26	22
33	DBP+PA-6 = 73,5 + 27,7 (mg)	370	26	16	35	29	20
34	DBP+PA-6 = 76,3 + 40,6 (mg)	370	20	10	38	27	25
35	DBP+PA-6,6 = 75,7 + 19,5 (mg)	350	20	30	31	23	16
36	DBP+PA-6,6 = 76,3 + 21,9 (mg)	370	20	27	34	21	18
37	DBP+PA-6,6 = 74,3 + 41,3 (mg)	370	20	8	36	28	28
38	DBP+PAN = 79,5 + 18,7 (mg)	310	20	9	46,5	44	0,5
39	DBP+PAN = 72,7 + 22,6 (mg)	330	20	17	28	39	16
40	DBP+PAN = 74,6 + 24,4 (mg)	350	20	16	32	39	13