CHEMOSPHERE

Chemosphere 54 (2004) 1521–1531

www.elsevier.com/locate/chemosphere

Formation of PCDDs and PCDFs during the combustion of polyvinylidene chloride and other polymers in the presence of HCl

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Received 16 October 2002; received in revised form 9 July 2003; accepted 28 July 2003

Abstract

PVDC and three non-chlorinated polymers (PP, PET, and PA) were incinerated at 700–850 °C in a laboratory-scale quartz tubular furnace in the presence of HCl (ca. 500 ppm ≅ 0.8 mg/l), and the gas-phase formation of PCDD/Fs, their putative precursors and their homologue profiles were investigated. The addition of HCl had little or no apparent effect on the level of PCDD/Fs formation during PVDC combustion, and their homologue profiles were quite different from those of the three non-chlorinated polymers. With PVDC, O_8CDD and particularly O_8CDF were by far most prevalent, apparently as a result of the selective formation of the precursors. With each of the three non-chlorinated polymers, combustion at 800 °C or higher in the presence of HCl resulted in PCDD/Fs formation at levels equaling or exceeding those observed with PVDC. In trials made with one of them (PP) under the same conditions but using a large polymer sample (100 mg vs 20 mg in all other trials), the level of PCDD/Fs formation was far higher than with the smaller polymer samples, and thus demonstrated the importance of appropriate combustion conditions for polymer incineration.

Keywords: Polychlorinated dibenzo-*p*-dioxins (PCDDs); Polychlorinated dibenzofurans (PCDFs); Polychlorobenzenes (PCBzs); Polychlorophenols (PCPhs); Polyvinylidene chloride (PVDC); Polypropylene (PP)

1. Introduction

In our previous study (Ohta et al., 2001), it was found that the combustion of PVDC under appropriate conditions (800 °C or higher, 3 s or more residence time, sufficient mixing turbulence) resulted in extremely low levels of polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans (PCDD/Fs) formation, while combustion at 750 °C or less resulted in higher levels of PCDDs and particularly PCDFs formation. In the present study, we further examined the mechanism of this PCDD/Fs formation, in terms of the profiles of their homologues formation and those of their putative precursors during the PVDC combustion, and investigated the effects of gas-phase HCl on PCDD/Fs formation during the combustion of polypropylene (PP), polyethylene terephthalate (PET), and polyamide (PA), as well as PVDC.

In municipal incinerators, the combustion gases generally include HCl at concentrations of several hundred ppm or higher, originating from NaCl and other chlorides commonly found in waste materials. It is believed this may lead to the formation of PCDD/Fs during the incineration of materials having no chlorine (Lenoir et al., 1991). The formation of PCDD/Fs has

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doi:10.1016/j.chemosphere.2003.07.002

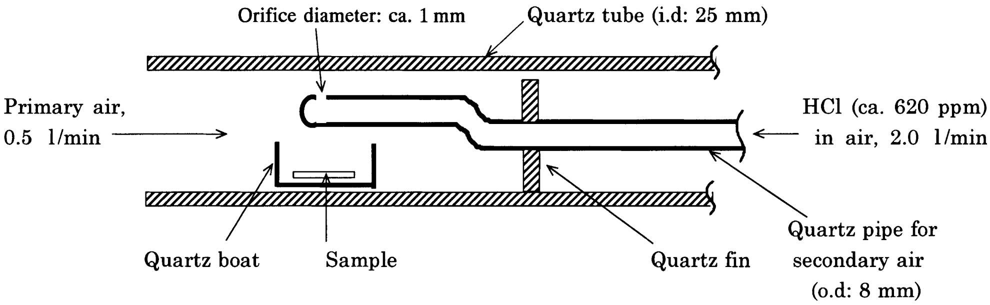

Fig. 1. First-stage combustion chamber.

been reported to occur during incineration of the hydrocarbons methane, propane, and ethylene in the presence of HCl (De Fre and Rymen, 1989). It has also been found to occur during the incineration of polyethylene, polystyrene, and polyurethane at low combustion temperatures (600 °C) in the presence of HCl at very high concentrations (130 mg/l) (Wirts et al., 1998).

Here we describe the results of our laboratory study on the combustion of PVDC, PP, PET, and PA in the presence of HCl at approximately 500 ppm (ca. 0.8 mg/l), and on the mechanism of PCDD/Fs formation in the light of their homologue profiles and those of their presumed polychlorobenzenes (PCBzs) and polychlorophenols (PCPhs) precursors.

2. Materials and methods

All experiments were performed at the facilities of Shimadzu Techno-Research Inc. (Kyoto, Japan).

2.1. Sample materials

The sample materials were the following commercially available films, having the indicated thicknesses: PVDC film, approximately 10 μm (Saran Wrap®, Asahi Kasei Corp., Tokyo, Japan); PP film, approximately 20 μm (Daicel Chemical Ind., Ltd., Osaka, Japan); PET film, approximately 20 μm (Futamura Chemical Ind. Co., Ltd., Nagoya, Japan); PA film, trilayer film consisting of nylon 6 (5 μm)/MXD [1] (5 μm)/nylon 6 (5 μm) (Mitsubishi Chemical Kohjin PAX Corp., Tokyo, Japan).

2.2. HCl

Approximately 620 ppm HCl in air (Takachiho Chemical Ind., Ltd., Tokyo, Japan).

2.3. Apparatus

As previously reported (Ohta et al., 2001), the apparatus consisted of a two-stage furnace containing a quartz tube, with a coaxial inner pipe to feed secondary air containing HCl to the first stage combustion zone (Fig. 1), and a collection unit comprised of a quench tube cooled by dry-ice and a tube packed with Amberlite® XAD-2. As shown in Fig. 1, the orifice in the inner pipe faced upward and was located vertically above the sample boat, to promote turbulence and thus mixing of the secondary feed air containing approximately 620 ppm HCl with both the primary feed air and the combustion gas.

2.4. Experimental conditions

Sample quantity: 20 mg per test, 50 repetitions per test run (total 1 g) for each of the four films; for the PP film also 100 mg per test, 10 repetitions per test run (total 1 g).
Air quantity: 2.5 l/min (primary, 0.5 l/min; secondary, 2.0 l/min).
HCl: approximately 500 ppm, calculated as 620 ppm × (2.0 l/2.5 l).
Combustion temperature: heater temperature settings of 700 °C in the first stage heater and 700, 750, 800, and 850 °C in the second stage heater.

2.5. Procedure

Before each test run, the quartz tube with no sample was held at the target temperature for 30 min with air feed and next for 30 min with nitrogen feed, and a blank test run lasting approximately 2 h was then performed at the target temperature with no sample.

For each of the four polymers, one test run consisted of 50 test repetitions with 20 mg of the sample per test and thus 1 g of sample per test run. For the PP film, a test run of 10 test repetitions with 100 mg per test, and thus 1 g per test run, was also performed to investigate

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[1] MXD: metaxylylenediamine/adipic acid copolymer.

the effects of incomplete combustion with non-chlorinated polymers.

The interval between test repetitions was approximately 1.5 min. Residence time in the second stage furnace was calculated as approximately 3 s at 800 °C, except in test runs in which a calculated residence time of approximately 2 s was obtained by using only three of its four heater units. The CO and O_2 concentrations in the combustion gas were monitored continuously, throughout the test runs.

2.6. Analysis

PCDD/Fs entrapped in the quench tube and the XAD-2 resin were determined by HRGC-HRMS, as described previously (Ohta et al., 2001).

PCBzs and PCPhs were determined by gas chromatography and mass spectrometry (GC-MS). The GC column was a DB-5MS (J&W) fused silica capillary column of 60 m (length), 0.32 mm (i.d.), and 0.25 μm (film thickness). The temperature program was 60 °C for 3 min, next to 110 °C at 5 °C/min, then to 265 °C at 8 °C/min.

3. Results and discussion

The results of the tests with 20-mg samples and thus generally complete combustion are presented in Section 3.1–3.5. The results of the tests with 100-mg PP samples, which were performed to investigate the effects of incomplete combustion in the presence of HCl, are presented in Section 3.6.

3.1. PCDD/Fs formation

The levels of PCDD/Fs formation in the test runs for all four polymers are summarized in Tables 1 and 2. The results clearly show the formation of PCDD/Fs during the combustion of non-chlorinated PP, PET, and PA in the presence of HCl. For PVDC, the presence of HCl had little effect on the PCDD/Fs level, presumably because the local concentration of HCl generated during PVDC combustion is itself quite high and thus little affected by the presence of HCl in the air at several hundred ppm.

The temperature dependence of the PCDD/Fs formation with PVDC was clearly different from that with the other three polymers (Fig. 2). The levels of formation with PVDC were clearly higher than with the other polymers during combustion at 700 and 750 °C, but about the same or lower than with the other three at 800 and 850 °C. With the three non-chlorinated polymers, particularly PET and PA, higher levels of PCDD/Fs formation than the blank test runs were observed even at 800 °C or higher. The results expressed in TEQ (Table 2) show that the formation of PCDD/Fs with PVDC was very low and nearly equal to those found in the blank test runs at 800 °C or higher, but with PET and PA it was clearly higher than the blank test runs.

In the test runs at 700 and 750 °C, moreover, the weight ratio of PCDFs to PCDDs was 300 or more with PVDC, but 10 or less with PP, PET, and PA (Table 1).

3.2. PCBzs and PCPhs formation

The levels of PCBzs (Cl = 3–6) and PCPhs (Cl = 3–5) formation found during combustion of each of the four polymers in the presence of HCl are shown in Table 3. The results for PVDC combustion in air with no HCl addition, which are also shown for reference, followed the same basic pattern as those found with PVDC in the presence of HCl.

The level of PCBzs formation with PVDC was high at 700 °C but declined with increasing combustion temperature, and at 850 °C was about the same as those found with the other three polymers, which showed much less change over the combustion temperature range of 750–850 °C and were thus much less temperature dependent.

The level of PCPhs formation was about the same for all four polymers over the temperature range of 750–850 °C, and was less temperature dependent than that of PCBzs.

The ratio of PCBzs to PCPhs was very high (in the range of 100–1000) with PVDC at all temperatures except 850 °C, but not far from 1 for the three other polymers at all temperatures.

3.3. Homologue profiles

The homologue profiles of the PCDD/Fs and their presumed PCBzs/PCPhs precursors, as found in the combustion test runs with 20-mg samples of each of the four polymers in the presence of HCl, are shown in Figs. 3 and 4, respectively. Also shown are the profiles observed with PVDC in air alone (for reference) and with the 100-mg PP samples.

With PVDC, the level of PCDFs generation was generally higher than that of PCDDs. As shown in Fig. 3, all of the PCDF homologues (tetrachloro- to octachlorodibenzofuran; T_4CDF to O_8CDF) were generated in large quantities at 700 °C, but O_8CDF generation was far larger than that of the other homologues at both 750 and 800 °C. With the other three polymers, all of the PCDD/F homologues were generated at all of the combustion temperatures.

A similar trend was observed among the homologues of the precursor PCBzs and PCPhs, as shown in Fig. 4. With PVDC, the generation of the PCBz homologue hexachlorobenzene (H_6CBz) was far larger than that of any of the other PCBz and PCPh homologues. With PP,

Table 1
PCDD/Fs formation (pg/g sample) during PVDC, PP, PET, and PA combustion

	700 °C			750 °C			800 °C			850 °C		
	PCDDs	PCDFs	DFs/DDs wt ratio	PCDDs	PCDFs	DFs/DDs wt ratio	PCDDs	PCDFs	DFs/DDs wt ratio	PCDDs	PCDFs	DFs/DDs wt ratio
PVDC 20 mg × 50 in air r.t. = 2 s	5300 (520)	1 730 000 (196 000)	326	230 (99)	150 000 (130 000)	652	21 (12)	1500 (1300)	71	180 (42)	880 (210)	4.5
	4600 (510)	1 600 000 (190 000)	348	420 (270)	170 000 (150 000)	405	38 (23)	640 (540)	17	28 (18)	300 (220)	11
PVDC 20 mg × 50 in HCl gas r.t. = 3 s	1800 (830)	560 000 (170 000)	311	490 (360)	150 000 (140 000)	306	97 (80)	9500 (9100)	98	57 (11)	150 (49)	2.6
	3100 (1300)	1 100 000 (340 000)	355	500 (430)	130 000 (130 000)	260	63 (50)	2400 (2300)	38	19 (8)	91 (66)	4.8
	2600 (1000)	800 000 (180 000)	308	310 (220)	99 000 (90 000)	319	68 (56)	1000 (930)	15	30 (14)	170 (87)	5.7
PP 20 mg × 50 in HCl gas r.t. = 3 s	1900 (1300)	10 000 (4900)	5.3	2700 (1800)	11 000 (5700)	4.1	690 (470)	2500 (1500)	3.6	140 (47)	850 (220)	6.1
	810 (430)	4200 (970)	5.2	2100 (380)	3500 (1100)	1.7	830 (600)	2600 (1500)	3.1	94 (46)	510 (170)	5.4
PP 100 mg × 10 in HCl gas r.t. = 3 s	15 000 (4500)	130 000 (23 000)	8.7	8700 (1800)	87 000 (12 000)	10	23 000 (6000)	200 000 (32 000)	8.7	52 000 (14 000)	470 000 (68 000)	9.0
	11 000 (3200)	95 000 (18 000)	8.6	4500 (750)	63 000 (6600)	14	10 000 (2100)	130 000 (16 000)	13	27 000 (7400)	310 000 (58 000)	11
PET 20 mg × 50 in HCl gas r.t. = 3 s	18 000 (11 000)	81 000 (29 000)	4.5	4100 (2800)	22 000 (14 000)	5.4	2300 (1800)	13 000 (9400)	5.7	730 (330)	4300 (1100)	5.9
	6300 (3900)	31 000 (15 000)	4.9	1000 (510)	3900 (2400)	3.9	270 (120)	1600 (450)	5.9	540 (190)	2900 (570)	5.4
PA 20 mg × 50 in HCl gas r.t. = 3 s	1900 (1000)	18 000 (7000)	9.5	1200 (690)	9800 (5800)	8.2	2900 (2100)	18 000 (12 000)	6.2	1100 (820)	6000 (3700)	5.5
	3100 (2000)	21 000 (8000)	6.8	1400 (870)	8100 (5400)	5.8	1400 (760)	6800 (3400)	4.9	360 (190)	1600 (900)	4.4

Blank in	29	230	7.9	180	930	5.2	78	400	5.1	40	270	6.7
HCl gas	(9.3)	(41)		(58)	(190)		(30)	(72)		(18)	(59)	
r.t. = 3 s	160	630	3.9	160	620	3.9	27	200	7.4	30	230	7.7
	(57)	(15)		(49)	(130)		(16)	(48)		(12)	(38)	

Multiple data represent the results of two or three test runs. Figures in parentheses are octachlorodibenzodioxin or octachlorodibenzofuran (pg/g sample).

PET, and PA, both H_6CBz and pentachlorophenol (P_5CPh) were generated in relatively large quantities, but the other precursor homologues were also generally observed.

3.4. *Characteristics of PCDD/Fs formation with PVDC*

It is known that in combustion processes resulting in the generation of PCDD/Fs, the level of PCDFs formation generally tends to be higher than that of PCDDs formation. With PVDC, this tendency was particularly strong, presumably as a result of the large quantity of PCBzs formed in combustion of this polymer. In other words, a high level of PCBzs formation leads to a high level of PCDFs formation.

Among the PCDD/F homologues generated with PVDC, the ratios of formation were relatively large for O_8CDD and O_8CDF. This is presumably attributable to the extremely high level of H_6CBz and, among the PCPh homologues, the relatively high level of P_5CPh formation.

3.5. *PCDD/Fs formation with PP, PET, and PA*

In the presence of HCl, the combustion of PP and particularly PET and PA resulted in levels of PCDD/Fs formation that were clearly higher than those of the blank test runs, even at 800 °C or higher. The reasons for this are not entirely clear, but the overall reaction pathway presumably consist of (1) formation of low-molecular-weight hydrocarbons and aromatics, as thermal decomposition products of the polymers (2) formation of precursors (PCBzs, PCPhs) by chlorination, molecular growth reactions, and cyclization of the hydrocarbons and by chlorination of the aromatics, and (3) formation of PCDD/Fs from these precursors. The time required for completion of this chain of reactions is relatively long, in comparison with PVDC, and the time remaining for their decomposition in our test furnace may therefore have been insufficient. These results appear to underline the importance of both the pathway and the location of the PCDD/Fs formation in the combustion gas stream.

The differences which were observed between the levels of PCDD/Fs formed at various temperatures with PP and those formed with PET and PA may be related to the presence of the aromatic ring in PET and PA and its absence in PP, leading to higher levels of PCDD/Fs formation with the PET and PA.

3.6. *PCDD/Fs formation with 100-mg PP*

Although the level of PCDD/Fs formation was generally low in the combustion test runs with 20-mg PP samples in air containing HCl, it became far higher with

Table 2
PCDD/Fs formation (pg-TEQ/g sample) during PVDC, PP, PET, and PA combustion

	700 °C	750 °C	800 °C	850 °C	Note
PVDC[a] 20 mg × 50	6800	39	5.6	0.44	In air r.t. = 3 s
PVDC 20 mg × 50	12 000, 12 000	180, 180	1.8, 1.0	20, 0.83	In air r.t. = 2 s
PVDC 20 mg × 50	4000, 6600, 5600	100, 87, 95	4.1, 1.0, 1.1	2.3, 0.1, 1.4	In HCl (500 ppm) r.t. = 3 s
PP 20 mg × 50	110, 62	91, 72	15, 18	16, 7.0	In HCl (500 ppm) r.t. = 3 s
PP 100 mg × 10	2400, 1700	1700, 1300	4300, 2700	9800, 6100	In HCl (500 ppm) r.t. = 3 s
PET 20 mg × 50	870, 270	140, 31	50, 22	77, 53	In HCl (500 ppm) r.t. = 3 s
PA 20 mg × 50	220, 250	68, 52	100, 75	42, 17	In HCl (500 ppm) r.t. = 3 s
Blank[b]	4.8, 14	17, 13	8.4, 3.2	5.6, 4.0	In HCl (500 ppm) r.t. = 3 s

Multiple data represent the results of two or three test runs.

[a] Details of the results are shown in the previous report (Ohta et al., 2001).

[b] 2 h duration was taken as equivalent to test run with 1 g of sample.

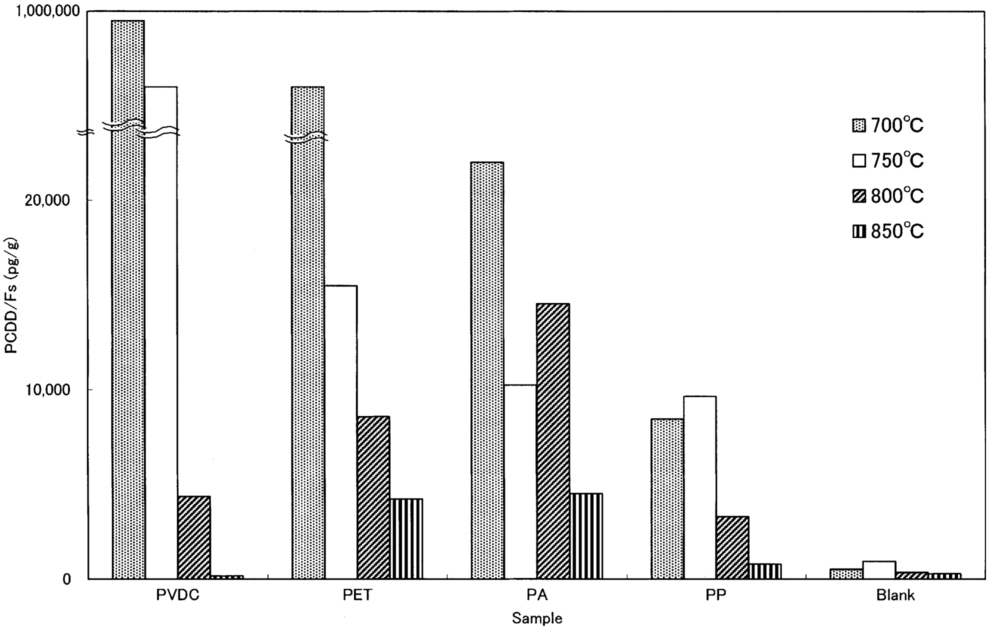

Fig. 2. PCDD/Fs formation (pg/g sample) during combustion of four polymers (20-mg samples) based on the mean value from the two or three test runs.

100-mg PP samples under the same conditions, and showed a clear tendency to increase with increasing combustion temperature (Tables 1 and 2). Under these incomplete combustion conditions, the formation of their precursor PCBzs and PCPhs also increased, particularly at the higher combustion temperatures (Table 3). This may be due to the rapid combustion rate which causes the increase of the extent of incomplete combustion. The increased precursor formation was thus directly related to the large quantities of PCDD/Fs formed with the 100-mg samples.

Soot formation was observed in the combustion with the 100-mg PP sample, but it is not clear whether the soot played any role in the increased levels of PCDD/Fs formation. It presumably contained no metals (e.g., Cu or Fe) which would exert a catalytic effect, and would therefore be expected to have little or no role in de novo synthesis of PCDD/Fs. It may be noted, however, that some studies have indicated the possibility that soot itself may have a catalytic effect (Luijk et al., 1994).

3.7. Pathways to PCDD/Fs formation with PVDC

Many studies have been reported on the generation and emission of PCDD/Fs in municipal incineration and other combustion of plastic resins, involving either homogeneous gas-phase reactions or post-furnace processes involving fly ash.

Table 3
PCBzs (Cl = 3–6) and PCPhs (Cl = 3–5) formation (ng/g sample) during PVDC, PP, PET, and PA combustion

Sample		700 °C	750 °C	800 °C	850 °C	Note
PVDC	PCBzs	250 000 (110 000)	96 000 (95 000)	4800 (4700)	240 (240)	In air
20 mg × 50	PCPhs	1100 (310)	100 (62)	44 (44)	30 (30)	r.t. = 2 s
	Ratio[a]	230	960	110	8.0	
PVDC	PCBzs	150 000 (100 000)	76 800 (76 000)	6450 (6400)	208 (190)	In HCl (500 ppm)
20 mg × 50	PCPhs	365 (170)	111 (42)	48 (14)	142 (35)	r.t. = 3 s
	Ratio[a]	415	692	134	1.5	
PP	PCBzs	280 (180)	180 (130)	74 (68)	71 (63)	In HCl (500 ppm)
20 mg × 50	PCPhs	610 (350)	170 (110)	27 (27)	<20 (<20)	r.t. = 3 s
	Ratio[a]	0.46	1.1	2.7	>3.6	
PP	PCBzs	540 (190)	350 (130)	880 (300)	2600 (690)	In HCl (500 ppm)
100 mg × 10	PCPhs	810 (290)	760 (200)	570 (200)	1700 (650)	r.t. = 3 s
	Ratio[a]	0.67	0.46	1.5	1.5	
PET	PCBzs	400 (280)	150 (120)	100 (86)	100 (77)	In HCl (500 ppm)
20 mg × 50	PCPhs	510 (320)	160 (130)	150 (110)	72 (26)	r.t. = 3 s
	Ratio[a]	0.8	0.94	0.67	1.4	
PA	PCBzs	250 (160)	150 (110)	180 (140)	110 (89)	In HCl (500 ppm)
20 mg × 50	PCPhs	230 (130)	110 (71)	150 (110)	100 (56)	r.t. = 3 s
	Ratio[a]	1.1	1.4	1.2	1.1	

Figures in parentheses show H_6CBz or P_5CPh (ng/g sample).

[a] PCBzs (Cl = 3–6)/PCPhs (Cl = 3–5) wt ratio.

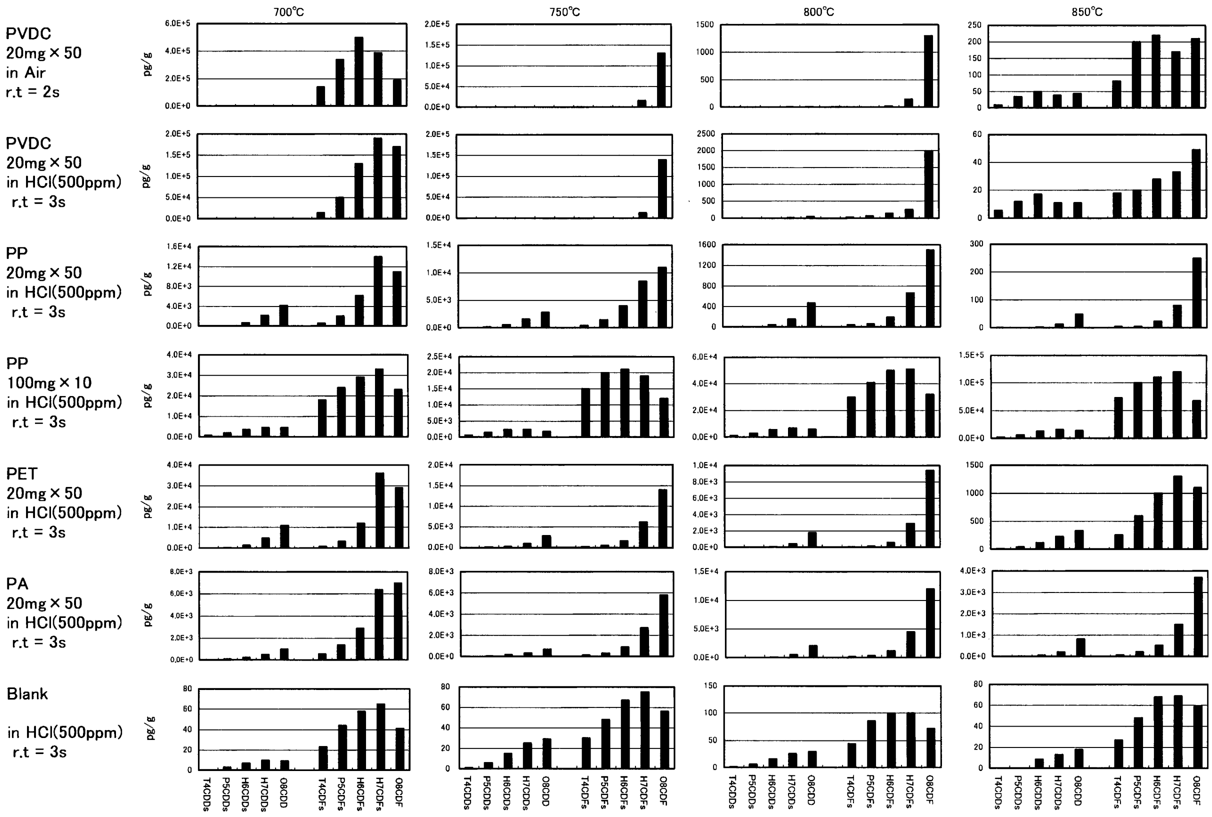

Fig. 3. PCDD/F homologue profiles of four polymers.

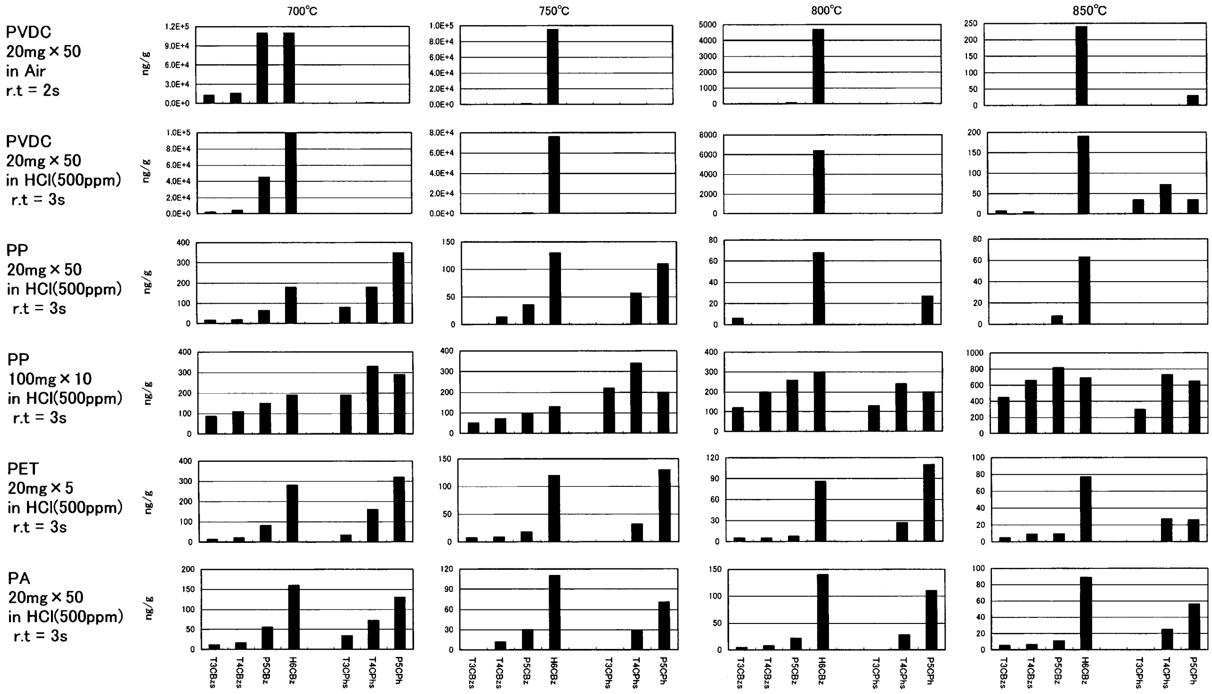

Fig. 4. PCBz/PCPh homologue profiles of four polymers.

Various studies have reported on post-furnace formation, since Lustenhouwer et al. (1980) first proposed mechanisms for PCDD/Fs formation. Many of these have focused on formation from precursors (Dickson and Karasek, 1987; Karasek and Dickson, 1987; Born et al., 1989; Dickson et al., 1989; Dickson et al., 1992; Born et al., 1993; Addink et al., 1995; Cains et al., 1997). Others have investigated de novo synthesis from carbon, organic fragments, and organic or inorganic chloride compounds (Stieglitz et al., 1989a,b; De Leer et al., 1989; Jay and Stieglitz, 1991). In their extensive review of reports then available, Huang and Buekens (1995) discussed the rates and mechanisms of post-combustion PCDD/Fs formation. Weber and Hagenmaier (1999b) performed an extensive investigation of the isomer distribution patterns of PCDD/Fs, PCBzs, and PCPhs in the flue gas, stack gas, and fly ash of fluidized bed incinerators, and concluded that the mechanism of PCDDs and PCDFs formation essentially consists of condensation reactions between PCPhs and between PCPhs and PCBzs respectively.

A model mechanism of homogeneous gas-phase formation of PCDDs from PCPhs was first proposed by Shaub and Tsang (1983). Ballschmiter and Swerev (1987) and Ballschmiter et al. (1988) subsequently reported on the mechanisms of PCDD/Fs formation by gas-phase reaction, in which they proposed PCBzs and PCPhs, and also polychlorobiphenyls and polychlorodiphenyl ether, as the main precursors.

Young and Voorhees (1991) discussed the mechanisms of incomplete combustion product formation in their investigation on pyrolysis of 1,2-dichlorobenzene. In a very early work, Buser (1979) described the formation of PCDD/Fs and PCPhs in PCBzs gas-phase pyrolysis (620 °C), and reported the formation of PCBz with higher-order chlorination than the starting PCBz, and PCDFs in quantities larger than those of PCDDs.

Menad and Björkman (2000) have reviewed both the gas-phase and the fly ash formation of PCDD/Fs from precursors, in the light of the reports available to that time.

In the past several years, in particular, various studies have stressed the importance of radical/radical reactions by PCPhs in the gas-phase formation of PCDD/Fs (Weber and Hagenmaier, 1999a; Wiater and Louw, 1999; Wiater et al., 2000; Wiater-Protas and Louw, 2001; Louw and Ahonkhai, 2002).

Other recent studies on the mechanism of gas-phase PCDD/Fs formation from PCPhs suggest that chlorophenoxyl radical/radical recombination reactions play an important role, and an elementary reaction-kinetic model has been developed (Evans and Dellinger, 2003; Khachatryan et al., 2003a,b).

In the present study on gas-phase PCDD/Fs formation, PVDC combustion resulted in the formation of large quantities of PCBzs, particularly those with a high order of chlorination. The large quantities of highly chlorinated benzenes (H_6CBz) and phenols (P_5CPh) may be the result of chlorine rearrangement reactions and thermal decomposition of homologues with lower-order chlorination. In the homologue profiles specific in this study to PVDC combustion at 750 and 800 °C, O_8CDF was predominant and among PCDD homologues, O_8CDD was highest (Table 1, Fig. 3). These profiles correlated closely with the patterns of precursor formation that were also found to be specific to PVDC combustion at these temperatures, in which H_6CBz accounted for nearly all of the PCBzs formation and the ratio of P_5CPh formation to that of other PCPhs was also very high (Table 3). In the PVDC combustion at 700 °C, in contrast, all of the tri- to hexa-chlorobenzene homologues were detected (T_3CBz, 13 μg/g; T_4CBz, 16 μg/g; P_5CBz, 110 μg/g; H_6CBz, 110 μg/g), as were all of the tri- to penta-chlorophenol homologues (T_3CPh, 0.30 μg/g; T_4CPh, 0.41 μg/g; P_5CPh, 0.31 μg/g), and formation of the T_4CDF to O_8CDF homologues found in this experiment is most likely attributable to reactions between these PCBzs and PCPhs.

In this light, the experimental results suggest that the formation of PCDFs in the combustion of PVDC throughout the temperature range of 700–800 °C is the result of chlorophenoxy radical-chlorobenzene reactions. This is in contrast to the conclusions of other studies which did not specifically consider PVDC combustion, that PCDFs formation occurs primarily by ortho–ortho coupling of chlorophenoxy radicals (Mulholland et al., 2001; Wiater-Protas and Louw, 2001; Louw and Ahonkhai, 2002).

In the combustion experiments with PP, PET, and PA, on the other hand, the quantity of PCBzs detected was extremely small (Table 3), indicating that the PCDD/Fs formation with these non-chlorinated resins was the result of gas-phase reaction between the precursor chlorophenoxy radicals.

4. Conclusion

In the combustion of PVDC at 750 and 800 °C in air with or without HCl addition, the PCDD/F homologues O_8CDD and particularly O_8CDF were formed in the highest quantities, apparently as a result of the high level of their precursor PCBz/PCPh homologues H_6CBz and P_5CPh. This PCDD/F homologue profile was specific to PVDC, and was not found to occur in the combustion of any of the other polymers under the same conditions.

These results indicate that in gas-phase reactions of PVDC combustion at high temperatures (700–850 °C), the formation of PCDD/Fs occurs via the formation of PCBzs, PCPhs, and perhaps other precursors.

PCDD/Fs were also found in the combustion of PP, PET, and PA in the presence of HCl under similar conditions. Under inappropriate combustion conditions, as shown by the results of the combustion tests using 100-mg samples of PP, the incineration of non-chlorinated polymers in the presence of HCl even at temperatures of 800 °C or higher may result in high levels of PCDD/Fs formation. It is therefore important to meet the three essential combustion conditions of appropriate temperature, residence time, and air mixing, in the incineration of non-chlorinated plastics as well as PVDC.

The results of the experiments with PP, PET, and PA in the presence of HCl indicate that PCPhs play the primary role in the formation of PCDD/Fs during combustion of these non-chlorinated polymers, in contrast to the results with PVDC.

Acknowledgements

We are grateful to Shimadzu Techno-Research Inc. for the use of their facility for the combustion experiments, and for the invaluable suggestions and guidance of Mr. Norihito Umezu and Mr. Takumi Takasuga relating to the planning of the experiments, operation of the facility, and evaluation of the results.

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