Low Flammability and Thermal Decomposition Behavior of Poly(3,3′-dihydroxybiphenylisophthalamide) and Its Derivatives

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ABSTRACT: The low flammability of poly(3,3′-dihydroxybiphenylisophthalamide) (PHA) and its halogen, methoxy, phosphinate, or phosphate derivatives was characterized by multiple analytical techniques, emphasizing the thermal decomposition behavior is the basis for the polymer flammability. Pyrolysis gases from these polymers were identified by pyrolysis GC/MS. The residual chars were characterized by elemental analysis. Simultaneous thermal analysis was applied to study the thermal decomposition process, and flammability was measured by a milligram-scale pyrolysis−combustion flow calorimeter (PCFC). It has been found that PHA and its halogen derivatives have extremely low flammability. They all exhibit a two-stage thermal decomposition process, where the first stage corresponds to cyclization into a quasi-poly(benzoxazole) (PBO) structure and the second stage is the random scission of the PBO backbone. However, the methoxy, phosphinate, and phosphate derivatives exhibit very different behaviors in thermal decomposition and flammability. Most of the PHAs produce a large amount of char, around 40−50%. Thermal decomposition mechanisms of PHAs were also proposed.

Introduction

The most efficient way to prevent polymer combustion is to design inherently fire-resistant polymers which have high thermal stability, resistance to the spread of flame, and low burning rate even under high heat flux.[1] Most polymers with high thermal stability are intrinsically fire-resistant. Because of their high decomposition temperatures, the initial breakdown will be effectively delayed, and the combustion process will not be initiated as easily as for other polymers.

There are three general types of structures for intrinsic fire-resistant polymers: (1) linear single-strand polymers having a sequence of cyclic aromatic or heterocyclic structures; (2) ladder polymers; (3) inorganic or semiorganic polymers.[2] So far, most carbon-based fire-resistant polymers are prepared by incorporating highly stable, rigid aromatic, or heterocyclic rings directly into the polymer chain,[3] such as polyimide (PI), polybenzoxazole (PBO), polybenzimidazole (PBI), and polybenzothiazoles (PBZT). Because all of these polymers contain a large number of aromatic groups in their structures and have strong tendencies to condense into chars upon heating, they produce lower amounts of flammable gaseous products during decomposition. The synthetic routes to such aromatic heterocyclic polymers typically involve a two-step process. Soluble high-molecular-weight prepolymers are generated first, and then rigid stable rings are formed by thermally or chemically induced condensation of reactive groups on the polymer chains.

Polybenzoxazoles (PBOs), which consist of alternating phenylene and condensed aromatic heterocyclic rings, have not only high thermal stability and low flammability but also good chemical resistance, high modulus, and high strength.[4−6] The first PBO was synthesized by Brinker and co-workers.[7] Later, Moyer[8] and Kubota[9] reported the preparation of fully aromatic PBOs by polycondensation reaction to yield the precursor poly(hydroxyamides) (PHAs), followed by thermal cyclodehydration to poly(benzoxazole) structures. However, these PBO polymers are infusible and are soluble only in concentrated sulfuric acid and polyphosphoric acid, so they are difficult to process. Thus, high costs of the finished polymers and of specialized fabrication techniques greatly limit their applications. Later, the effects of introducing “hinge” atoms or groups into the polymer chain were investigated to increase their flexibility. For example, incorporation of fluorinated linking groups into the polymer backbone enhanced solubility, while good thermooxidative stability and high glass transition temperature were retained.[10,11]

However, not very much research has been performed on the precursor poly(hydroxyamide) or PHA. Pearce et al. have reported detailed investigations on the syntheses, thermal properties, and oxygen index of a series of wholly aromatic polyamides based on substituted and unsubstituted *m*- or *p*-phenylenediamine with both isophthaloyl and terephthaloyl chlorides.[12−16] They found that the ortho- halogen-, nitro-, and cyano-substituted polyamides produce the highest char yield which are due to cross-linking at high temperatures and the formation of thermally stable benzoxazole rings.[15,17−22] The amount of PBO structure formed was dependent on the nature of the substituents. The more electron-withdrawing the substituent, e.g., F or NO_2, the more benzoxazole structure is formed. Recently, Kantor et al.[23] have synthesized a high-molecular-weight poly(3,3′-dihydroxybiphenylisophthalamide) (PHA) as well as a series of its halogen, methoxy, phosphinate, and phosphate derivatives. It is found that this PHA can not only cyclize into fire-resistant PBO but also absorb some heat and liberate noncombustible water vapor during cyclization.[24,25] In addition, all these polymers show a very good solubility in aprotic solvents such as *N*-methylpyrrolidinone (NMP), *N*,*N*-dimethylacetamide (DMAc), and

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N,*N*-dimethylformamide (DMF). Therefore, they are potential candidates as solvent-processable fire-resistant polymers for many high-performance applications.

To discover new fire-resistant polymers and understand how and why polymers burn, small-scale experimental techniques suitable for research quantities have to be developed. Standard tests such as the Underwriter Laboratories Test for Flammability of Plastic Materials (UL-94), limiting oxygen index (LOI), and cone calorimetry all require relatively large amount of samples (at least tens of grams), and the test results are determined not only by the characteristics of the materials but also by many other conditions and factors. Therefore, these test methods can be used only as a guide. Pyrolysis–combustion flow calorimetry (PCFC) is a very new, rapid, and quantitative milligram-scale flammability test.[26–28] It is operated on the oxygen consumption principle that cone calorimetry exploits; i.e., the net heat of complete combustion of typical organic molecules is relatively constant per mole of oxygen consumed, $E = 419 \pm 19$ kJ/mol of $O_2 = 13.1 \pm 0.6$ kJ/g of O_2, essentially independent of the chemical composition of the combusted materials. Requiring only milligram samples, PCFC is an efficient screening tool for the newly synthesized fire-resistant materials.[29] Generally, samples are pyrolyzed in an inert gas stream, followed by high-temperature combustion of the volatiles in excess oxygen. The heat release rate, total heat of combustion of the volatiles, and char yield can all be obtained from PCFC. In addition, PCFC results correlate well with standard tests such as UL-94 test, oxygen bomb calorimetry (ASTM D2382), and cone calorimetry at 50 kW/m^2 incident heat flux (ASTM E1354).[30] Nevertheless, a combination of technologies is essential to understand the complex issues of the fire resistance of the polymers because the thermal decomposition processes of polymers are varied and complicated, and the flammability properties of a particular fire-resistant polymer are dependent on the test method used.

In this paper, three major experimental techniques—pyrolysis–combustion flow calorimetry (PCFC), simultaneous thermal analysis (STA), and pyrolysis GC/MS—have been combined to fully characterize the thermal decomposition and flammability of PHA and its halogen, methoxy, phosphinate, and phosphate derivatives. Halogen, phosphinate, and phosphate derivatives were examined because of their expected flame-retardant effects, while methoxy derivatives were examined because of their easy syntheses. Thermal decomposition mechanisms were also proposed for these polymers.

Experimental Section

Materials. The chemical structures of PHA and its derivatives are given in Scheme 1. All the samples were supplied by Kantor's group at the University of Massachusetts, Amherst.[23]

Characterization. The thermal decomposition process was examined under N_2 or air by a TA Instruments 2050 thermogravimetric analyzer (TGA). Simultaneous thermal analysis (STA) was also performed under N_2 with a Rheometric Scientific STA 1500 to study the mass change and the heat absorbed or evolved during the decomposition at high temperatures. Char yield of the polymers is defined here as the percentage of solid residue at 930 °C under N_2. Sample weights for all the thermal analyses were approximately 10 mg, and the heating rate was 10 °C/min.

Flammability of all the polymers was measured with a PCFC.[26–28] Samples of 1.0 ± 0.1 mg were pyrolyzed in a commercial device (CDS Pyroprobe 2000) to 930 °C at 4.3 °C/s under N_2. The volatiles were swept out continuously by a N_2 flow, mixed with a metered flow of O_2, and completely combusted at 900 °C. Consumption rate of O_2 was measured continuously. The heat release results were taken as the average of five measurements for each sample.

Composition of the volatiles was analyzed by pyrolysis GC/MS. Samples of 0.2–0.3 mg were pyrolyzed to 930 °C at 4.3 °C/s in helium. The volatiles from pyrolysis were then separated by a Hewlett-Packard 5890 Series II gas chromatograph and analyzed by a Hewlett-Packard 5972 Series mass spectrometer. A fused silica capillary GC column (cross-linked 5% PH ME siloxane, 0.25 mm in diameter and 30 m long) was used. The GC oven was programmed from 36 to 295 °C at a heating rate of 10 °C/min and then held at 295 °C for 15 min. Masses were scanned from m/z 11 to 550.

Elemental analyses were obtained on a Control Equipment model 240XA elemental analyzer.

Results and Discussion

Thermal Stability and Decomposition Processes of PHAs. Table 1 summarizes the thermal decomposition of PHA and its derivatives. The following discussion examines details of their different decomposition behaviors.

PHA-1 and -2 all decompose in two distinct and well-separated stages, but PHA-2 (para) is more thermally stable than PHA-1 (iso) due to its regular symmetric structure. X-ray diffraction results (Figure 1) proved that PHA-2 has a higher crystallinity than PHA-1.

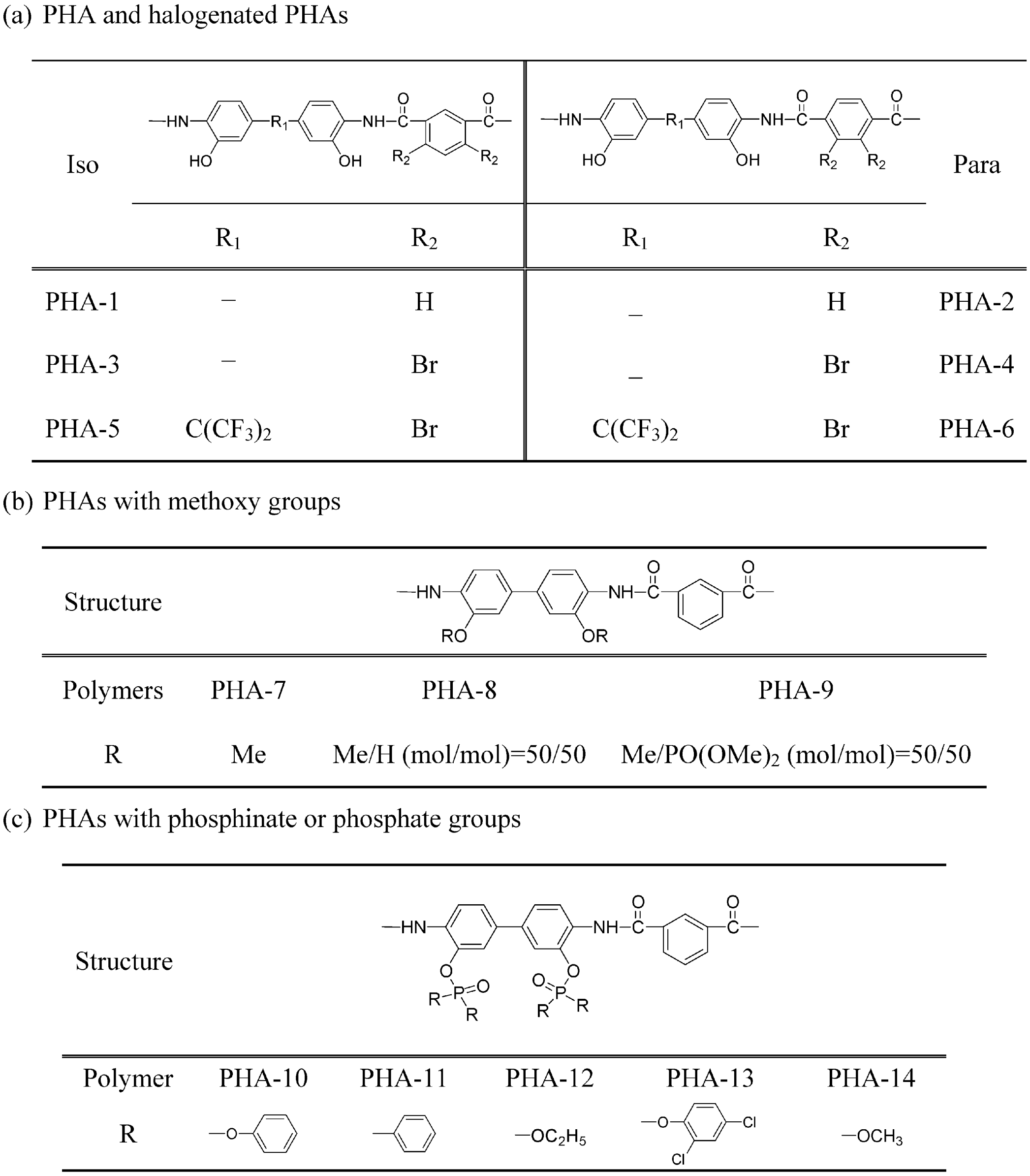
It was found that the thermal decomposition process, flammability, and decomposition products of corresponding iso- and para-type PHAs are all similar to each other except that para-PHAs have higher thermal stability. Only the flammability and thermal decomposition properties of iso-PHAs will be discussed below.

The thermal decomposition processes of PHA-1 and its derivatives under N_2 are shown in Figure 2. According to Figure 2a, PHA-1 lost about 11% weight in the first decomposition stage, which agrees very well with the calculated 11.5 wt % water loss due to the cyclization reaction. The second stage is associated with a further 30% weight loss due to the extensive breakdown of the polymer backbone.

Halogenated PHAs (PHA-3 and -5) also decompose in two stages, which is similar to PHA-1 (Figure 2a). Introduction of bromine groups in PHA-3 slightly decreases the thermal stability of the first stage (240 °C). In contrast, trifluoromethyl groups have the effect of increasing the thermal stability of PHA-5 (274 °C). However, the onset decomposition temperature of the second stage is greatly reduced in both PHA-3 (485 °C) and PHA-5 (508 °C) compared with PHA-1 (586 °C). This is because the halogenated PBOs formed at the end of the first stage are less stable. At high temperatures, the halogen groups can be easily stripped off from the phenyl rings before any backbone scission.

In PHA-7, hydroxyl groups are totally replaced by methoxy groups. PHA-7 is quite stable up to about 363 °C, but then it has a sharp weight loss between 363 and 469 °C (Figure 2b). 40% weight loss in the first stage is apparently not due to the analogous PHA-to-PBO cyclization reaction, in which methanol would be released, but it is mainly due to the release of 1,3-dimethyl isophthalate, which is shown in Figure 6. Copolymer PHA-8 with both methoxy and hydroxyl groups shows three stages of decomposition. The first stage (240–335 °C) is due to the cyclization of hydroxyl groups (6 wt % water loss as expected). The second stage (397–476 °C) is related to the decomposition of the structures con-

Scheme 1. Structures of PHA and Its Derivatives



(a) PHA and halogenated PHAs

Iso	R_1	R_2	R_1	R_2	Para
PHA-1	–	H	–	H	PHA-2
PHA-3	–	Br	–	Br	PHA-4
PHA-5	$C(CF_3)_2$	Br	$C(CF_3)_2$	Br	PHA-6

(b) PHAs with methoxy groups

Polymers	PHA-7	PHA-8	PHA-9
R	Me	Me/H (mol/mol)=50/50	Me/$PO(OMe)_2$ (mol/mol)=50/50

(c) PHAs with phosphinate or phosphate groups

Polymer	PHA-10	PHA-11	PHA-12	PHA-13	PHA-14
R			$-OC_2H_5$		$-OCH_3$

Table 1. Thermal Decomposition of PHA and Its Derivatives (in N_2)

polymers	η_{inh}[a]	$T_{99\%}$ (°C)[b]	T_2 (°C)[c]	ΔW_1 (%)[d]	ΔH_1 (J/g)[e]	ΔT (°C)[f]
PHA-1	0.60	250	586	11	116	240−383
PHA-2		290	622	10	145	270−456
PHA-3	0.49	240	485	13	106	250−400
PHA-4		284	515	12	110	260−430
PHA-5	0.25	274	508	8	104	245−356
PHA-6		282	501	7	108	260−360
PHA-7	0.62	363	591	37		363−469
PHA-8	0.70	240	592	6	105	240−335
PHA-9		218	574	7	33	230−310
PHA-10	0.44	270	640	45		210−500
PHA-11	0.55	300	606	56		270−545
PHA-12	*g*	182	651	16	72	180−360
PHA-13	*g*	200	654	21	106	180−306
PHA-14	*g*	184	652	23	121	180−370

[a] 0.5 g/dL in NMP at room temperature. [b] Temperature at 1% weight loss. [c] Onset decomposition temperature of the last stage. [d] Weight loss during the first stage. [e] Heat absorbed during the first stage. [f] Temperature range of the first stage. [g] Polymers are only partially soluble in NMP.

taining methoxy groups, and the third stage is the high-temperature decomposition of polymer main chain.

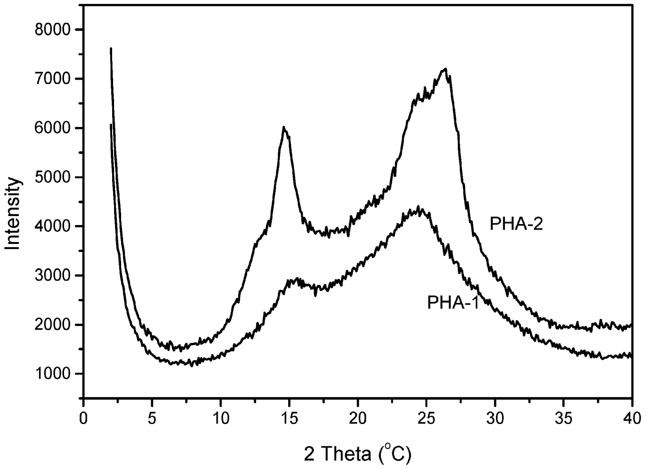


Figure 1. X-ray diffraction of PHA-1 and -2.

Thermal stability of PHA-9 is very low due to the presence of large phosphate groups ($-PO_2(OMe)_2$). Although PHA-7, -8, and -9 have different side groups, they all show a similar decomposing stage between 570

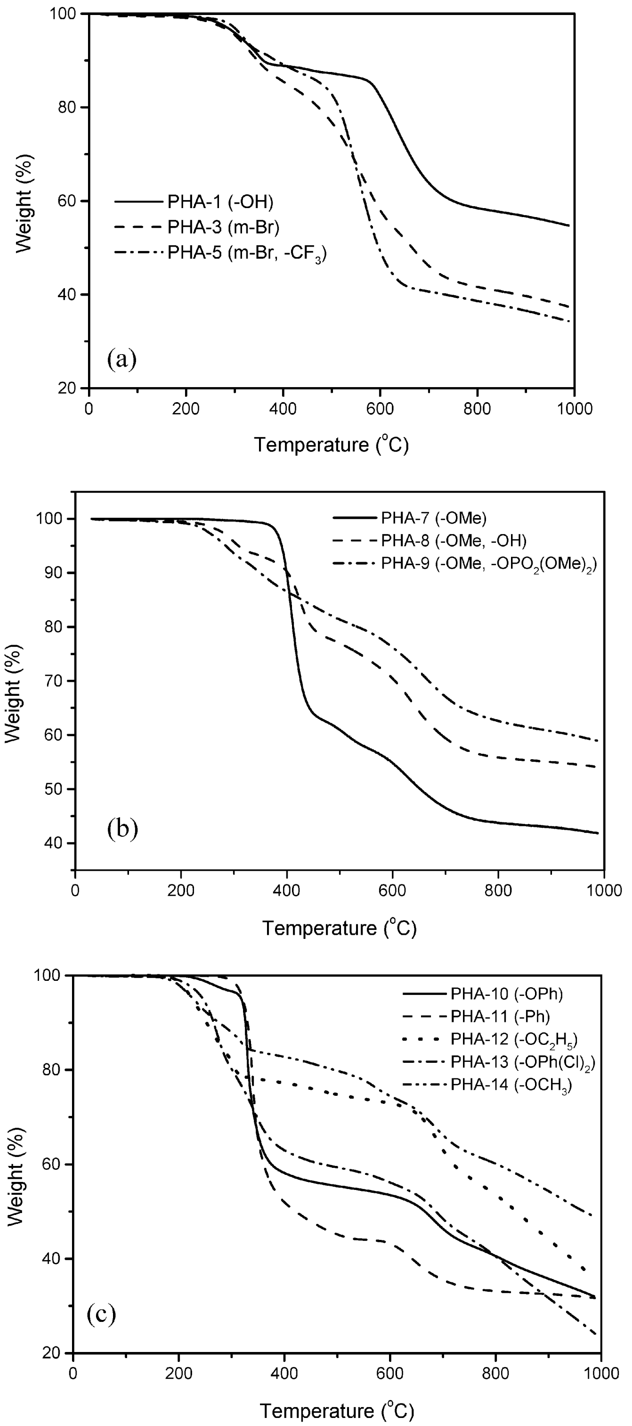


Figure 2. TGA curves of PHA-1 and its derivatives (in N$_2$): (a) PHA-1 and halogenated PHAs; (b) PHAs with methoxy groups; (c) PHAs with phosphinate or phosphate groups.

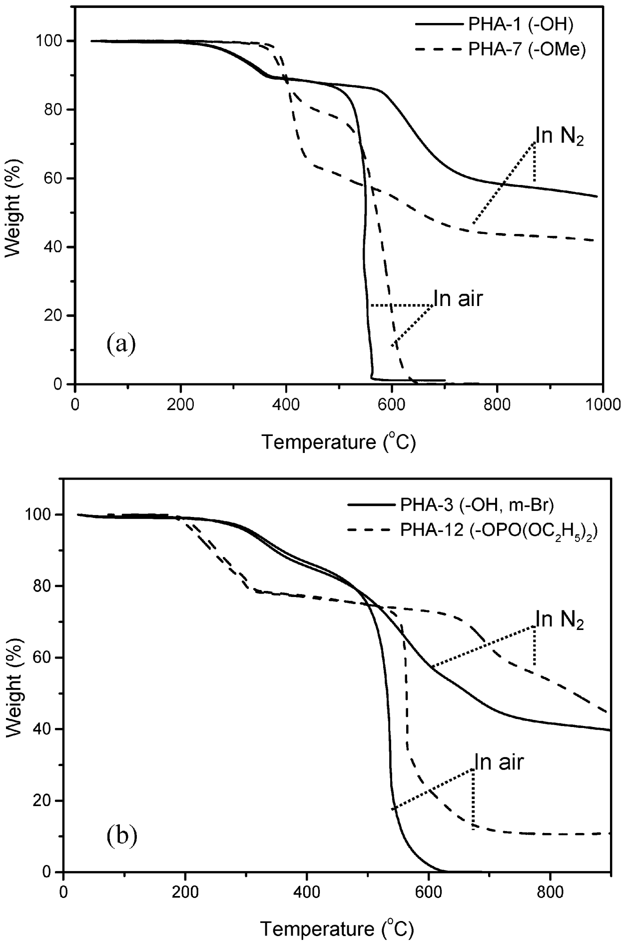


Figure 3. Effects of oxygen on the thermal decomposition of PHA-1 and its derivatives: (a) PHA-1 and its methoxy derivative; (b) halogenated and phosphate PHAs.

and 800 °C, which is due to the decomposition of one particular structure.

The thermal decomposition processes of PHA-10 to -14, which contain different phosphinate or phosphate groups, are very different from each other (Figure 2c). PHA-10 and PHA-11 have relatively high thermal stability (300 °C) due to their relatively strong bonds in phosphinate or phosphate groups. However, PHA-12 to -14 start to lose weight around 180 °C. It is believed that at low temperatures (180−500 °C) the main decomposition is the cleavage of phosphinate or phosphate groups from polymer main chain due to their relatively weak linkages and further decomposition of these phosphiantes and phosphates. At high temperatures (above 500 °C), the polymers break along the main chain. Similar to PHA-1 and PHA-7 to -9, these phosphinate or phosphate PHAs all start a new decomposition step around 600 °C, which suggests that all these PHAs are converted into a similar structure before 600 °C.

In N$_2$ atmospheres, all the PHAs can produce high char yields. Char can act as a thermal and mass transfer barrier and greatly reduce the flammability of polymers. However, when PHAs are heated in air, the TGA curves are somewhat different (Figure 3). Although oxygen has no effect on the first decomposition stage, it reduces the thermal stability of the second stage except for the PHAs with halogen groups. Above 600 °C, all the PHAs except for those with phosphinate or phosphate groups completely burn up without any char left. It can be concluded that oxygen does not affect the initial thermal stability, but it can oxidize the carbonaceous char very easily at high temperatures. The halogen groups can improve the thermooxidative stability, while phosphinate or phosphate groups can preserve more chars during burning.

Besides the thermal stability and decomposition processes, another important thermal property that can be obtained only by STA measurements is the enthalpy change associated with the weight loss. The STA measurement is a very good method to study the heat of decomposition because it can perform TGA and DSC at the same time up to 1500 °C. The high-temperature

Table 2. Flammability of PHA and Its Derivatives

polymers	HR capacity[a] (J/(g K))	total heat[a] (kJ/g)	T_{max}[b] (°C)	max mass loss rate ($\times 10^3$/s)	char yield (%)
PHA-7	130	17	409	1.4	43
PHA-1	42	10	633	0.4	56
PHA-8	33	11	425	0.5	55
PHA-9	18	9	658	0.2	60
PHA-3	17	5	563	0.4	39
PHA-5	8	3	553	0.7	36
PHA-10	340	15	327	3.3	36
PHA-11	210	21	341	2.9	32
PHA-12	73	9	304	0.4	41
PHA-13	59	8	271	0.6	29
PHA-14	19	8	319	0.2	52
PE[c]	1558	40	471	7.0	0
PS[c]	1199	37	417	5.2	0
PC[c]	382	19	514	3.3	17
Kevlar[c]	292	15	576	2.5	32
PEEK[c]	163	13	586	2.2	46
PI[c]	29	9	602	0.5	50

[a] PCFC results. The rest are TGA results. [b] The temperature at maximum mass loss rate. [c] Commercial polymers. PE = polyethylene; PS = polystyrene; PC = BPA−polycarbonate; PEEK = poly(ether ether ketone); PI = polyimide.

DSC curves of PHA and its derivatives are shown in Figure 4.

All the PHAs (except for PHA-10 and -11) show an endothermic peak in the early stage of decomposition, but they differ at high temperatures. In the case of PHA-1, -3, and -5 (Figure 4a), the heat absorbed in the first stage is around 105−120 J/g as a consequence of the cyclization reaction and vaporization of the water. In the second stage, PHA-1 shows a combination of endo- and exothermic behavior which might be due to the combined effects of decomposition and char formation. PHA-3 and PHA-5 instead show a distinct exothermic peak in the second stage, which might be due to the release of HBr and some cross-linking reactions. For PHA-7 with methoxy groups (Figure 4b), the endothermic peak between 320 and 385 °C might result from the melting of the polymer because no significant weight loss is detected during that temperature range. The following exothermic peak (386−469 °C) is probably due to a series of thermal decomposition reactions, including some possible cyclization reactions and main-chain scissions. The heat events in phosphinate or phosphate PHAs (Figure 4c) are more complicated. PHA-12 to -14 show endothermic peaks at low temperatures (180−360 °C) due to the release and decomposition of phosphinate or phosphate side groups. However, PHA-10 and -11 have a combination of endo- and exothermic peaks in the first stage. The enthalpy changes of methoxy phosphinate or phosphate PHAs are difficult to determine at high temperatures.

Flammability. Flammability of these PHAs was measured with the PCFC.[26−28] Heat release rate of the volatiles (J/s) is calculated from the measured oxygen consumption, following signal deconvolution to correct for flow dispersion. Heat release capacity (J/(g K)), obtained by dividing maximum heat release rate by the sample weight and heating rate, is an important parameter for evaluating polymer flammability. The total heat of combustion (kJ/g) of the fuel gases per unit sample mass is obtained by direct integration of the heat release rate vs time. Char yield is determined by weighing the sample before and after the test, which is consistent with the TGA results. The coefficient of variation of heat release capacity is around 10%, and the systematic error for total heat released is around 1 kJ/g.

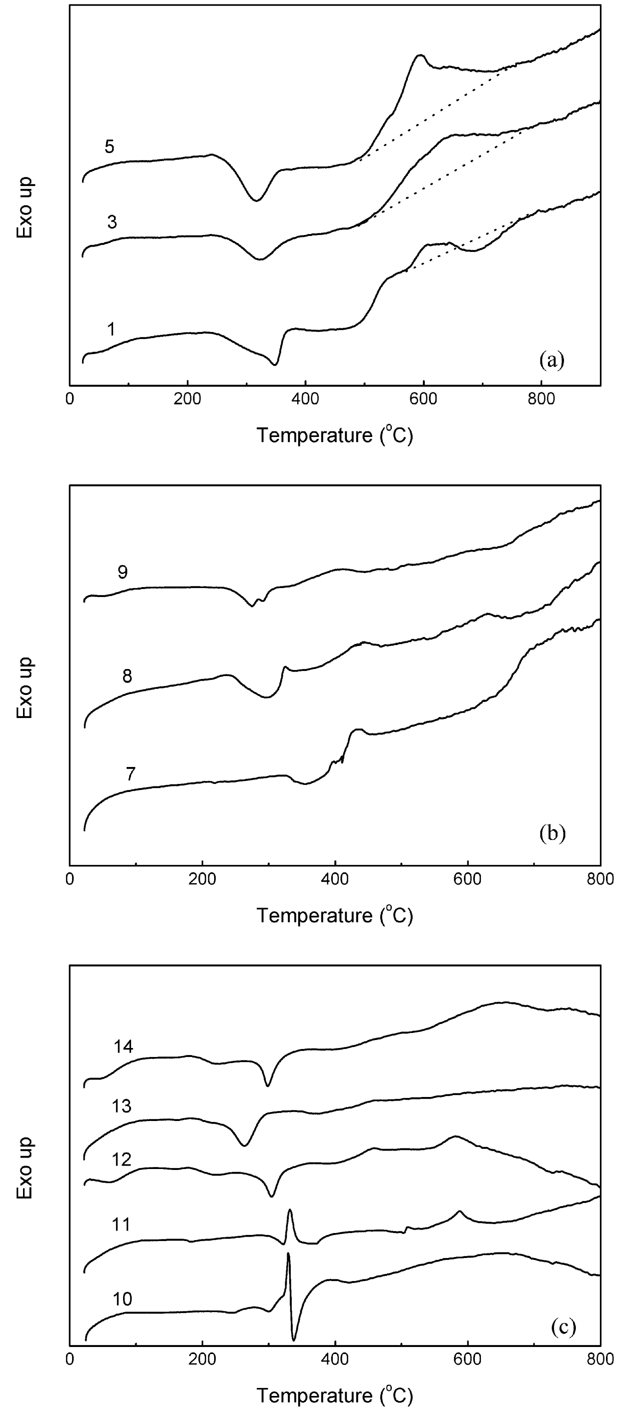


Figure 4. High-temperature DSC curves of PHA-1 and its derivatives: (a) PHA-1 and halogenated PHAs; (b) PHAs with methoxy groups; (c) PHAs with phosphinate or phosphate groups.

The PCFC results (Table 2) show that PHA and most of its derivatives have rather low flammability compared to some commercial polymers such as polyethylene (PE), polystyrene (PS), and polycarbonate (PC). Fire resistance of PHA-1 is close to polyimide. Moreover, bromine and trifluoromethyl groups can further reduce the flammability by releasing halogenated compounds. As a result, PHA-5 is one of the few polymers that have extremely low flammability. The flammability of PHA-7 is relatively high, but it can be reduced by partially

Table 3. Elemental Analyses of PHA-1 at Different Temperatures

	measured (wt %)				calculated (wt %)				
temp (°C)	C	H	N	O	C	H	N	O	residual weight (%)
25 (PHA)	67.26	3.78	7.56	21.4	69.4	4.1	8.1	18.4	100
400 (PBO)	75.96	3.26	8.62	12.16	77.4	3.2	9	10.4	90
650	79.97	2.93	7.84	9.26					75
1000	87.07	0.44	3.78	8.71					50

replacing methoxy groups with hydroxyl (PHA-8) or phosphate groups (PHA-9) to form a copolymer, which can extend the decomposition temperature range and slow down the decomposition rate.

However, if methoxy or hydroxyl groups are totally substituted by different phosphinate or phosphate groups (PHA-10 to -14), the flammability of polymers is greatly dependent on the types of phosphinate or phosphate groups. PHA-10 and -11, which contain phenyl or phenoxy groups in the phosphinate or phosphate, have relatively higher flammability. The higher flammability is due to their relatively faster decomposition rates and release of more flammable compounds such as benzene and phenol. The flammability of PHA-12 to -14 is greatly reduced due to their significant reduction in the mass loss rates. Therefore, the introduction of bulky phosphinate or phosphate side groups to a thermally stable PHA backbone does not always improve the flame resistance of the polymers even though the phosphinates or phosphates are widely used in the industry as flame-retardant additives for plastics. Worse, the flammability of the polymers might be increased due to the fast cleavage of these bulky fuel-forming side groups.

Generally, PHAs with low mass-loss rates usually have low heat release capacity (except for halogenated PHAs). This is because there are two factors that can determine the heat release capacity: maximum mass loss rate and the heat of combustion of the decomposition products at that temperature. For PHAs with similar structures, the major decomposition products are not very different. Therefore, the mass loss rate becomes the most important factor that can determine the heat release rate. According to Table 2, PHA-1 and halogenated PHAs (PHA-3 and -5) decompose faster at high temperatures (maximum mass loss rates occur around 550−650 °C) due to the massive main-chain scission, while PHA-7, PHA-8, and PHA-10 to -14 have their maximum mass loss rates at low temperatures (around 300−500 °C) due to main-chain scission or the fast cleavage of methyl, phosphinate, or phosphate groups.

Although PHA-8 is the copolymer of PHA-1 and PHA-7, its flammability is almost the same as PHA-1 rather than an average of the two homopolymers. This nonlinearity means that copolymerization of two polymers with different thermal stability, thermal decomposition process, and flammability might be an efficient way to reduce flammability. The copolymerization can broaden the whole decomposition range and reduce the mass loss rate, therefore reducing the heat release rate.

To summarize, the major reasons for the low flammability of most PHA polymers are the stable aromatic backbone structures, low mass loss rates, high char yields, and the ability to release flame-retardant molecules during decomposition (such as water and halogenated compounds) which can act physically or chemically during combustion. However, the introduction of bulky, fuel-forming phosphinate or phosphate groups should be avoided in order to get good flame resistance.

Characterization of Chars by Elemental Analysis. Chars are complex materials that contain fused aromatic structures and may include heteroatoms (O, N, P, S). They are usually insoluble, which limits their characterization to the tools used in solid-state chemistry and physics. The composition of the char is usually characterized by elemental analysis. Table 3 lists some elemental analyses of PHA-1 pyrolyzed at different temperatures.

According to Table 3, the char of PHA-1 at 400 °C has the same elemental composition as PBO, which supports the assumption that the first stage is due to the cyclization reaction. With temperature increasing, the contents of H, N, and O decrease dramatically, but the carbon content increases. At 1000 °C, the formula of the char can be written as $C_{27}H_{1.63}NO_2$, which suggests that the structure of the char at high temperatures must be some fused aromatic and heteroaromatic rings with low hydrogen content.

Identification of Volatiles by GC/MS. The volatiles from all the PHAs are characterized by pyrolysis GC/MS to aid the development of decomposition mechanisms. The total ion current (TIC) pyrograms of some PHAs are shown in Figure 5. All the volatiles can be divided into four groups: (1) low-boiling-point products such as CO, CO_2, H_2O, CH_3OH, and HCN, which cannot be separated effectively at the normal GC operation and may come from the cyclization reaction or decomposition of the backbone at high temperatures; (2) aromatic hydrocarbons, amines, acids, nitriles, benzoxazoles, and isocynates which correspond to the partial fragments from polymer main chain; (3) halogen, methyl, phosphinate, and phosphate compounds which are attributed to the cleavage of the side groups; (4) high-boiling-point products formed by isomerization, rearrangement, or cross-linking reactions at high temperatures, such as 3,4-diphenyl-1*H*-pyrazole.

About 70 wt % of volatiles ultimately released from PHAs (except for phosphinate or phosphate PHAs) are CO_2, CO, H_2O, and HCN, of which CO_2 and CO are present in the largest quantities (around 50 wt %). In contrast, major decomposition products of PHA-10−14 consist of phosphinates, phosphates, and their ester fragments such as phenol, benzene, 2,4-dichlorophenol, methanol, and ethanol. It is also found that HCN (about 5−10 wt %) is only produced at high temperatures, usually above 500 °C. With temperature increase, the CO/CO_2 ratio increases.

In PHA-3 and -5, bromine is observed in the volatiles not only as HBr but also in the form of a small amount of brominated aromatic compounds (such as $C_6H_4Br_2$ and $C_6H_3Br_3$). However, fluorine was only detected as fluorinated compounds (such as CF_3Br and CF_3CH_2Br). All these halogenated products have low heats of combustion on their own and are very good gas-phase flame retardants during combustion.

An important characteristic of the decomposition of PHAs with methoxy groups is that their decomposition products contain a significant amount of methyl- or methoxy-substituted aromatic compounds. The methyl or methoxy groups might come from the cleavage of side groups.

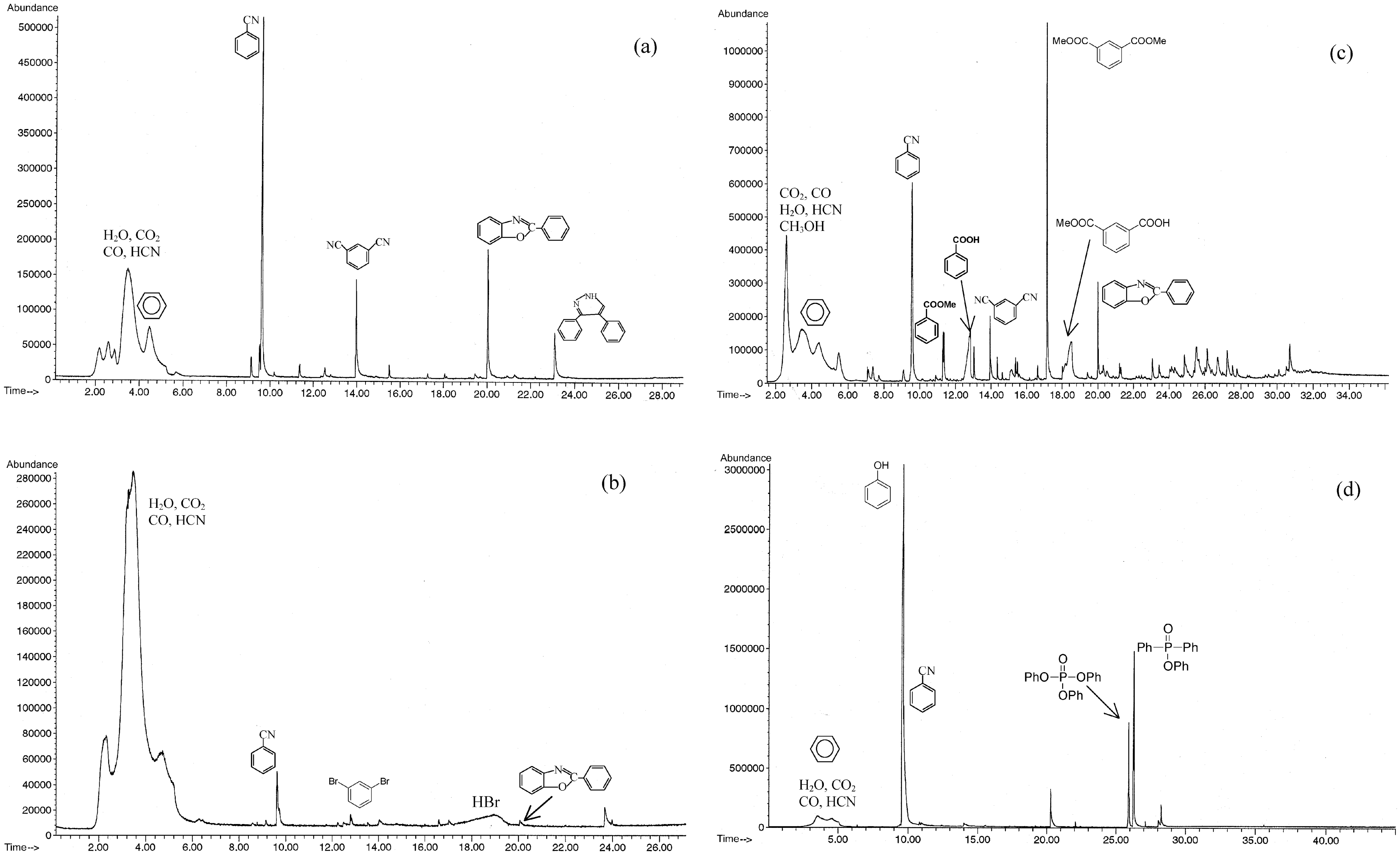


Figure 5. TIC pyrogram of PHA-1 and its derivatives (heating to 930 °C at 4.3 °C/s): (a) PHA-1; (b) PHA-3; (c) PHA-7; (d) PHA-10.

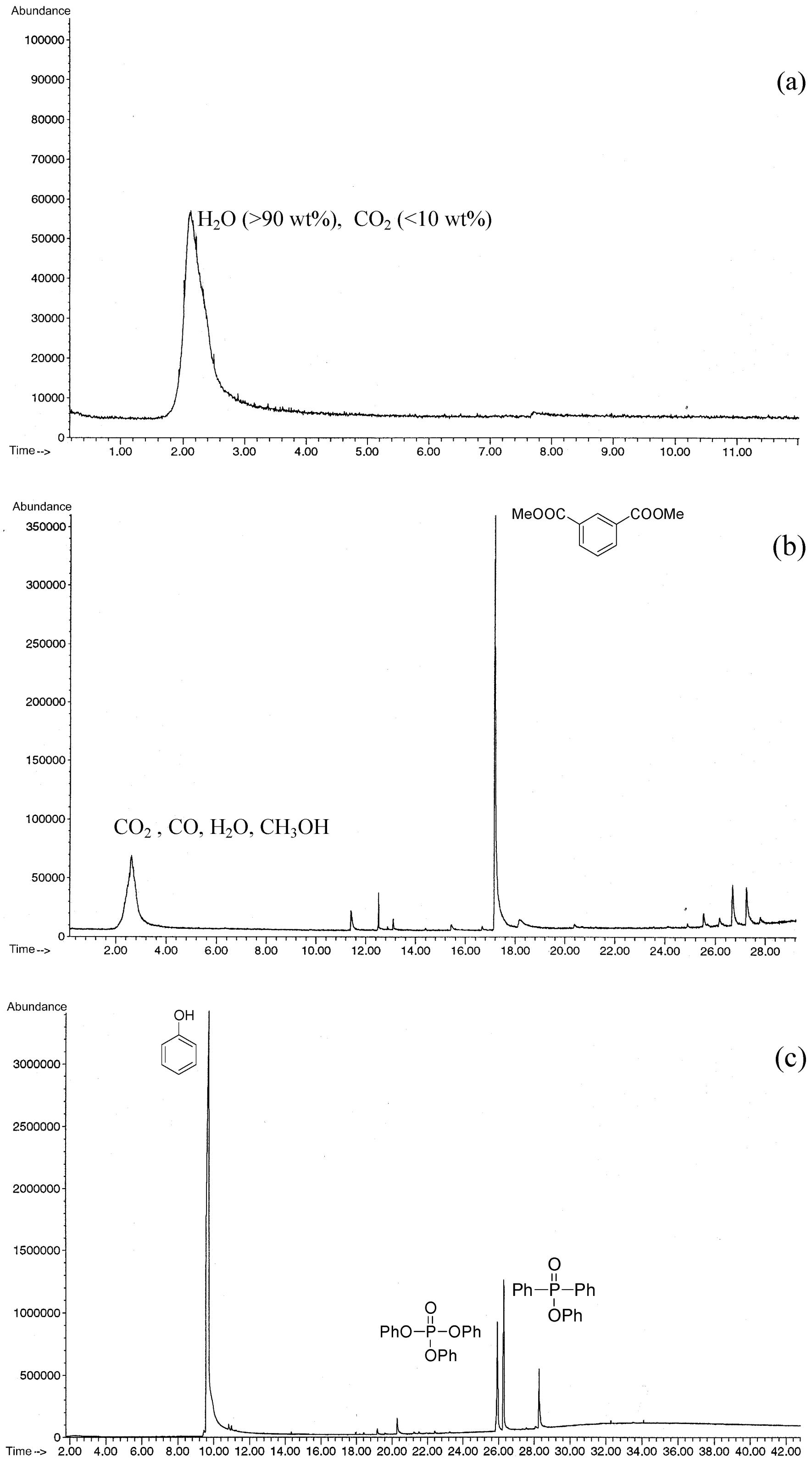
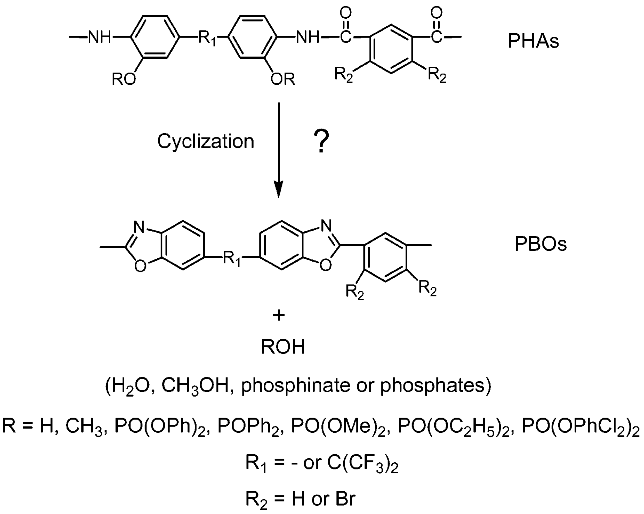


Figure 6. TIC pyrogram of PHAs at low temperatures (heating rate 4.3 °C/s): (a) PHA-1 (250−383 °C); (b) PHA-7 (350−469 °C); (c) PHA-10 (250−500 °C).

The thermal decomposition products at different temperature ranges were also studied. Figure 6 shows the volatiles released at low temperatures from several PHAs. For PHAs containing only hydroxy groups (PHA-1, -3, and -5), the main decomposition products during the first stage are water and a small amount of CO_2 which suggests some hydrolytic decomposition. The water generated during cyclization could be responsible for this hydrolysis. When these polymers are heated to higher temperatures, they release some aromatic compounds, such as the heterocyclic−aromatic species 2-phenylbenzoxazole, which is a typical structure within

Scheme 2. Presumed Cyclization of PHA and Its Derivatives



PBO. However, the major volatiles are still CO_2, CO, H_2O, and HCN, which along with high char yields are responsible for their low flammability.

In contrast, for PHAs with methoxy groups such as PHA-7, the decomposition products during the first stage contain not only CO_2, CO, H_2O, and CH_3OH but also a large amount of 1,3-dimethyl isophthalate. At higher temperatures, these polymers give out more aromatic compounds with methoxy or methyl substituents.

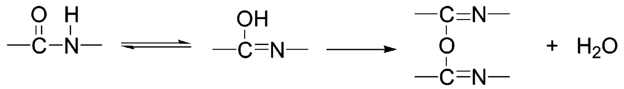
The major decomposition products of phosphinate or phosphate PHAs below 500 °C are flammable phosphinates and phosphates as well as their ester fragments, which lead to their high flammability. At high temperatures, some aromatic compounds are released.

In summary, at low temperatures (below 500 °C), most volatiles released are H_2O, CO_2, CH_3OH, phosphinates, phosphates, and their ester fragments depending on the structures of the PHAs. At high temperatures (above 500 °C), PHAs produce more aromatic volatiles as result of backbone scission.

Thermal Decomposition Mechanisms. Thermal decomposition mechanisms of PHA-1 and its different derivatives were proposed by identification of the major volatiles. The cycliztion of PHA-1 into PBO is well-known.[7-9] Pearce et al. have also studied the basic mechanisms for the formation of PBO's from ortho halogen-, nitro-, and cyano-substituted polyamides.[15,17-22] They found that the char yield and flame resistance of these polyamides can all be greatly improved due to the ring-forming reaction during their pyrolysis. However, there is no detailed research on the thermal decomposition of methoxy, phosphinate, or phosphate PHAs.

Possibly, PHA derivatives might decompose by the same mechanism as PHA-1, shown in Scheme 2. First, they are cyclized to PBO by releasing corresponding small molecules ROH. The PBO structures formed then break down at high temperatures. In the following discussion, we will investigate whether this mechanism is valid for all the PHA derivatives.

Scheme 3. Water Generated by Intermolecular Reaction



On the basis of the pyrograms of PHA-1 at low temperatures, water is the major volatile due to the intramolecular cyclization. On the other hand, H_2O could also be generated by the intermolecular condensation of iminol forms[17] (Scheme 3). However, this reaction has a lower probability of occurring because the presence of 2-phenylbenzoxazole in the high-temperature decomposition volatiles strongly suggests that H_2O is formed by intramolecular cyclization (Scheme 4a (I)).

A small amount of CO_2 detected in the first decomposition stage of PHA-1 might be due to the hydrolytic cleavage of the amide linkage, which can lead to the formation of two fragments with NH_2 and COOH end groups. The COOH groups would then decarboxylate to give out CO_2. This hydrolytic reaction is quite possible because a significant amount of H_2O is generated in this stage.

The second stage is the decomposition of the PBO structure formed. High-temperature thermal decomposition might be initiated by random homolytic cleavage of the strong phenyl−phenyl bond in the main chain, followed by hydrogen transfer, rearrangement, cross-linking, and some other secondary reactions.

PHA-3 and -5 decompose in almost the same way as PHA-1, but the amount of aromatic volatile is greatly reduced by the introduction of heavy bromine atom. HBr is formed in the second stage by homolytic cleavage of the aromatic C−Br bond, followed by hydrogen abstraction.

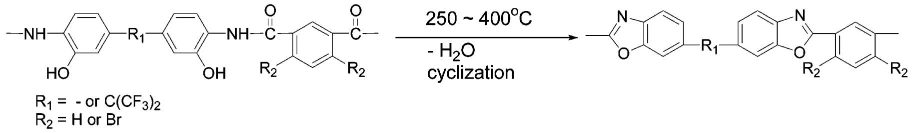
Although the only structural difference between PHA-7 and PHA-1 is OCH_3 vs OH side groups, their decomposition mechanisms are very different. The detection of 2-phenylbenzoxazole from PHA-7 above 500 °C indicates that some cyclization reactions occurred in the first decomposition stage. However, if PHA-7 is cyclized by the same mechanism proposed for PHA-1, about 17 wt % methanol should be released. However, only 1.5 wt % methanol is detected by GC/MS, and the 40% weight loss observed in the first stage is due to other compounds such as CO_2, CO, H_2O, and dimethyl isophthalate. The formation of dimethyl isophthalate can only be achieved by breaking the polymer main chain. Therefore, it is believed that both cyclization and main chain scission occurred in PHA-7 during first decomposition stage (Scheme 4a (II)). In addition, the cyclization reaction does not proceed by releasing methanol, but more likely through another route that releases water (around 5 wt % detected by GC/MS). Then, at the end of first stage, PHA-7 is converted into a structure with both benzoxazole rings and methoxy groups. Because both PHA-1 and PHA-7 have the same backbone structures, the difference in decomposition mechanisms must be attributed to the side groups. It is found that the O−Me bond (50 kcal/mol), the weakest bond in PHA-7, is much weaker than O−H bonds (72 kcal/mol) in PHA-1. As a result, the methyl groups can be easily cleaved from the polymer backbone and react with the aromatic radicals to form various methyl- or methoxy-substituted compounds.

Similarly, the bulky phosphinate or phosphate side groups in PHA-10−14 can be easily cut away from the polymer backbone at low temperatures due to their weak linkages (Scheme 4a (III)). Then following the same route as PHA-7, the polymers can be transformed into a structure with both benzoxazole rings and phosphinate or phosphate groups before any main-chain scission. According to elemental analysis, the char at

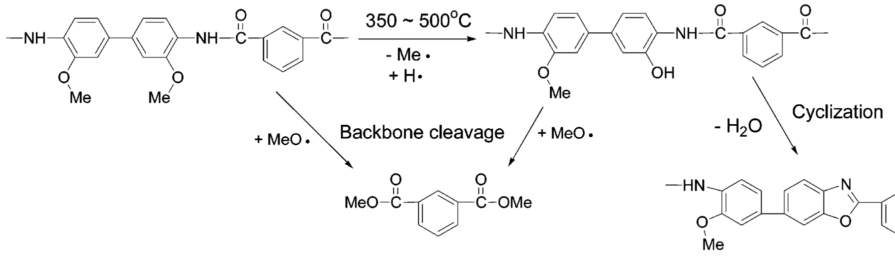
Scheme 4. Thermal Decomposition Mechanisms of PHAs

(a) Low temperatures (<500°C)

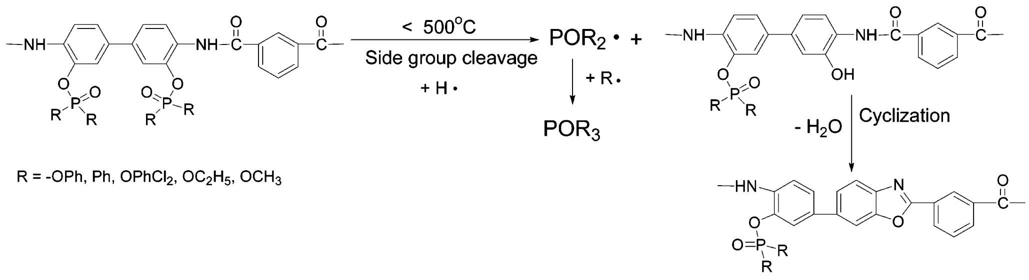
(I) PHA and halogenated PHAs (PHA-1, 3, 5)



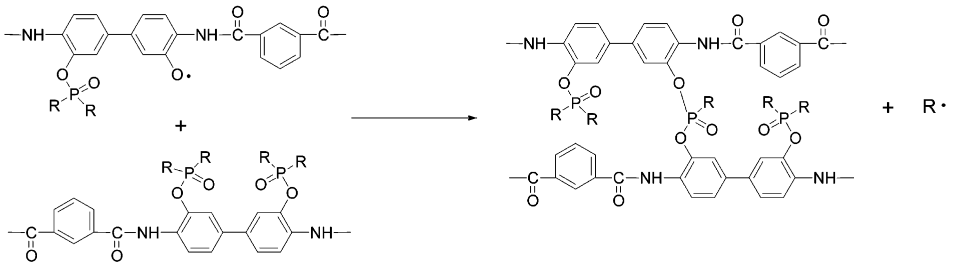
(II) PHAs with methoxy groups (PHA-7 ~ 9)



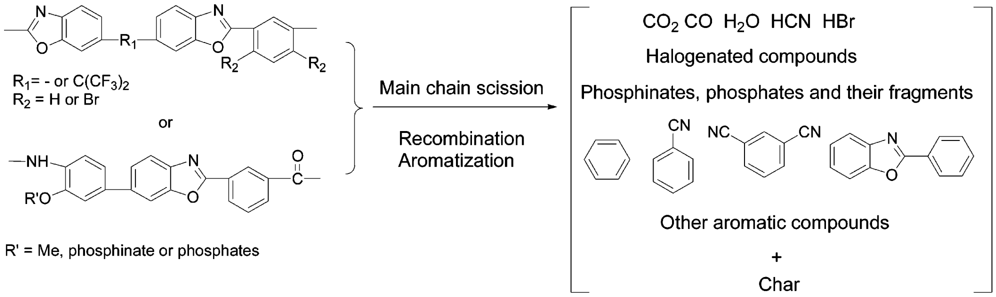
(III) Phosphinate or phosphate PHAs (PHA-10~14)



Cross-linking reaction



(b) High temperatures (>500°C)



930 °C still contain a certain amount of phosphorus, which might be trapped by some cross-linking reactions during decomposition. This observation proves that phosphorus can reduce flammability in the condensed phase by promoting the char formation.

At high temperatures (above 500 °C), the decomposition of methoxy and phosphinate or phosphate PHAs is basically due to the random main-chain scission of a general structure which contains both benzoxazole rings and methoxy, phosphinate, or phosphate groups (Scheme 4b). However, PHA and halogenated PHAs are totally converted into quasi-PBO structures at the end of first stage. Many reactions can occur at high temperatures, such as main-chain scission to give out different aromatic volatiles and recombination and aromatization to form char.

The thermal decomposition mechanisms of all the PHAs are summarized in Scheme 4.

Conclusions

PHA and most of its derivatives have very low flammability, especially the ones containing halogen groups. PHA-7 with methoxy groups is more thermally stable, but it exhibits higher flammability due to the main-chain scission at low temperatures. PHA-10 and -11 are also relatively flammable due to the extensive cleavage of fuel-forming phosphinate and phosphate side groups. The thermal decomposition process of the PHAs can be roughly divided into two stages. In the first stage (below 500 °C), small molecules such as water, methanol, phosphinate, or phosphates as well as their ester fragments are released to form some quasi-PBO structures. In the second stage (above 500 °C), the random scission of the polymer backbone will occur. Most PHAs show an endothermic peak at low temperatures, but due to different mechanisms such as cyclization, melting, and decomposition. Halogenated PHA-3 and -5 show a distinct exothermic peak at high temperatures due to the formation of HBr and some cross-linking reactions. Elemental analysis proves that the first decomposition stage of PHA-1 corresponds to cyclization into PBO. The major decomposition products of most PHAs (except for phosphinate or phosphate PHAs) are CO, CO_2, H_2O, HCN, and a small amount of aromatic compounds. The low flammable volatiles, low mass loss rates, and high char yields are the major reasons for their low flammability. Different from PHAs with hydroxyl groups, methoxy-, phosphinate-, or phosphate-substituted PHAs can only be partially cyclized into PBO structures.

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