



## Thermal degradation of deoxybenzoin polymers studied by pyrolysis-gas chromatography/mass spectrometry

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### ABSTRACT

The thermal degradation behavior of novel ultra-fire-resistant polymers and copolymers containing deoxybenzoin units in the backbone was studied by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). The polymers were synthesized by the polycondensation of 4,4'-bishydroxydeoxybenzoin (BHDB) with isophthaloyl chloride (to give polyarylates), phenylphosphonic dichloride (to give polyphosphonates), and their mixtures (to give poly(arylate-co-phosphonate) copolymers). The thermal decomposition, under nitrogen conditions, of BHDB-polyarylate was characterized by a simultaneous degradation of both the bisphenolic (deoxybenzoin) and isophthalate sub-units, whereas a three-step decomposition phenomenon was observed for the BHDB-polyphosphonate. BHDB-polymers containing phosphonate groups in the backbone did not show any phosphorus-based volatile decomposition products, whereas the corresponding bisphenol A-based polyphosphonates released volatile decomposition products comprised mainly of phosphorus-containing compounds.

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### 1. Introduction

The burning process of organic polymers comprises four main stages: heating, pyrolytic gas evolution, ignition, and flame-spread. Flame retardants are added to polymers to reduce their flammability. These additives, acting in either the vapor or condensed phases, interfere with the combustion process during one or more stages of the burning process. Halogenated organic molecules predominantly act in the vapor phase by free radical mechanisms to interrupt exothermic oxidative reactions and thereby limit combustion. On the other hand, non-halogenated flame retardants, such as phosphorus-based additives, mainly act in the condensed phase by promoting char formation on the surface of the material, which functions as a heat barrier, thus inhibiting further degradation. The environmental bio-accumulation and related health concerns associated with brominated flame retardants motivate researchers to develop halogen-free, inherently fire-resistant high-performance polymers [1–5]. We have recently identified a new bisphenolic monomer, 4,4'-bishydroxydeoxybenzoin (BHDB), for the preparation of anti-flammable polymers. Through step-growth polymerization, halogen-free polyarylates, polyphosphonates, and poly(arylate-co-phosphonate)s were synthesized from BHDB [6–8]. The heat release properties of

these polymers were studied by pyrolysis combustion flow calorimetry (PCFC), which has been established as a rapid, quantitative predictor of material flammability [9]. All the BHDB-based polymers exhibit low heat release capacity (HRC) values of <100 J/g K. These values are superior to those of many commercially available low-flammability polymers, such as polyvinylidene fluoride (311 J/g K), polyphenylene sulfide (165 J/g K), polyether ether ketone (155 J/g K), polyphenyl sulfone (153 J/g K), polyether imide (121 J/g K), and polyether sulfone (115 J/g K) [10].

The HRC values of BHDB-polyarylates and polyphosphonates compare favorably to the bisphenol A (BPA) versions used in the production of commercial thermoplastics and thermosets. HRC of BPA-containing polyarylates and polyphosphonates were ~380 and ~440 J/g K, respectively, while those of the corresponding BHDB-polymers are ~65 and ~80 J/g K [6,7]. Char yields obtained by TGA track similarly. BPA-polyarylate and polyphosphonate have char yields of ~30 and ~23%, respectively, whereas the corresponding values for the BHDB-polyarylates and polyphosphonates are ~45 and ~52%. The lower HRCs and higher char yields of BHDB-polymers may arise from thermally induced conversion of deoxybenzoin to diphenylacetylene moieties, which subsequently form char by cross-linking or aromatization [11,12].

Understanding thermal decomposition mechanisms of polymers is important for the rational design of anti-flammable polymers. The relative ratios of char and gaseous products determine, in large part, the flammability of a polymer material. Higher char yield

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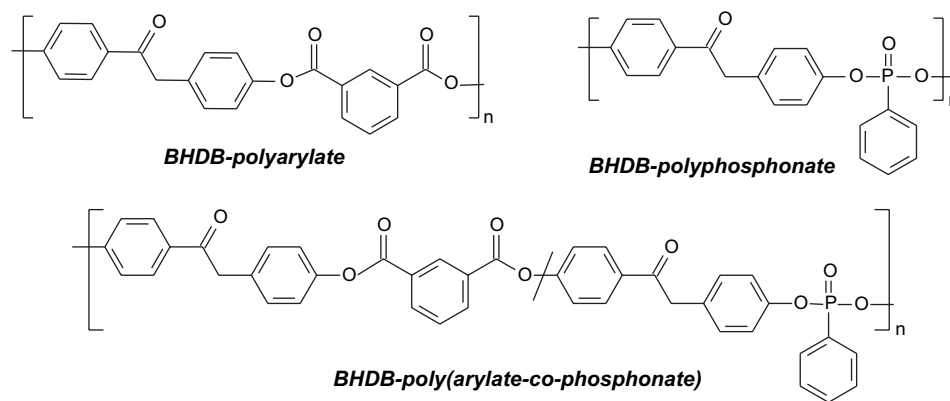


Fig. 1. Structures of BHDB-containing polymers analyzed in this study.

inhibits combustible gas release, decreases heat release, and inhibits thermal conductivity at the burning surface.

van Krevelen described a method to predict char formation from the chemical structures of various halogen-free polymers [13]. He also developed an empirical equation  $LOI = 17.5 + 0.4(CY)$  relating char yield (CY) and the limiting oxygen index (LOI), a numerical index defined as the minimum volume percent of oxygen, in an oxygen–nitrogen mixture, required to support downward burning of a vertically mounted test specimen [13]. Lower LOI values indicate higher flammability, and polymers exhibiting LOI values under 26 are considered flammable [14].

More mechanistic understanding may be obtained using pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS), which has been widely-employed for polymer analysis and characterization [15]. In Py-GC/MS, the polymer sample is pyrolyzed, and the volatile products generated are passed through a gas chromatography column for separation, and then characterized by mass spectrometry. This provides direct structural information about pyrolysis products as well as insight into bond-breaking, rearrangement, and decomposition mechanisms. Thus, Py-GC/MS is a tool for understanding thermal degradation, and corresponding flammability properties, of a material. Here, we apply Py-GC/MS to the decomposition mechanism of BHDB-based polyarylates and phosphonates, as well as poly(arylate-co-phosphonate) copolymers.

## 2. Experimental

### 2.1. Materials

The synthetic procedures and molecular characterization of BHDB-polymers (polyarylate, polyphosphonate, poly(arylate-co-phosphonate)s) can be found from our earlier publications [6–8].

**Table 1**  
Properties of BHDB-based polymers

Polymer	Molar ratios (isophthalate:phosphonate) <sup>a</sup>	GPC <sup>b</sup>	PCFC	TGA	Estimated LOI (%) <sup>e</sup>
		$M_w$ (g/mol) (PDI)	HRC (J/g K) <sup>c</sup>	Char yield (%) <sup>d</sup>	
P-0	100:0	15,100 (1.29)	65	45	36
P-23	77:23	65,600 (1.78)	48	50	38
P-43	57:43	50,700 (1.78)	41	56	40
P-54	46:54	54,600 (2.27)	36	54	39
P-61	39:61	83,700 (2.69)	40	57	40
P-77	23:77	61,000 (1.65)	59	55	40
P-100	0:100	92,700 (2.26)	80	52	38

<sup>a</sup> Ratio calculated by proton NMR integrations.

<sup>b</sup> GPC data in DMF solvent against polystyrene standards.

<sup>c</sup> Average over three runs.

<sup>d</sup> Measured at 800 °C.

<sup>e</sup> Calculated using the equation  $LOI = 17.5 + 0.4(CY)$  [13].

### 2.2. Characterization

Thermogravimetric analysis (TGA) was carried out in a DuPont TGA 2950, with heating to 900 °C at a rate of 10 °C/min under a nitrogen atmosphere. A sample weight of 3–5 mg was used. The volatile decomposition products were analyzed by pyrolysis GC/MS. Samples of 30–100 µg of the material were placed in a quartz tube (1 mm internal diameter × 13 mm length) and the ends were sealed with glass wool. The sample was then loaded in the pyrolysis probe (Pyroprobe 1000/2000) and placed in the special inlet in the interface. The samples were pyrolyzed successively at the required temperatures at 4.3 °C/s under helium atmosphere and kept at each temperature for 30 s. The volatiles were separated by a Hewlett–Packard 5890 Series II gas chromatograph and analyzed by a Hewlett–Packard 5972 Series mass spectrometer. A capillary GC column filled with cross-linked 5% PH ME siloxane, 0.25 mm in diameter and 30 m long, was employed. The GC oven was programmed from 40 to 295 °C at a heating rate of 10 °C/min and then held at 295 °C for 15 min. Masses were scanned from  $m/z$  16 to 550.

### 2.3. Quantum chemical calculations

The quantum chemical calculations of bond energies were completed using the B3LYP density function method [16–18], using the standard polarized split-valence 6-31G(d) basis set [19]. UB3LYP/6-31G(d) calculations should provide reasonable accuracy for the identification of likely reaction locations. This base density-functional method and modest basis set were chosen to

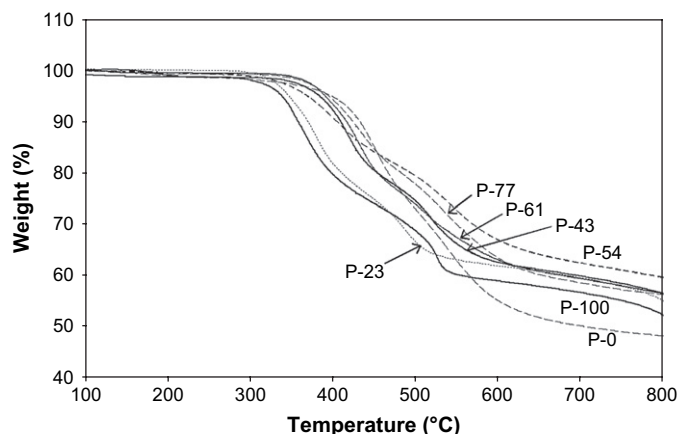


Fig. 2. TGA curves (under nitrogen atmosphere) for BHDB-containing polymers with various P-values.

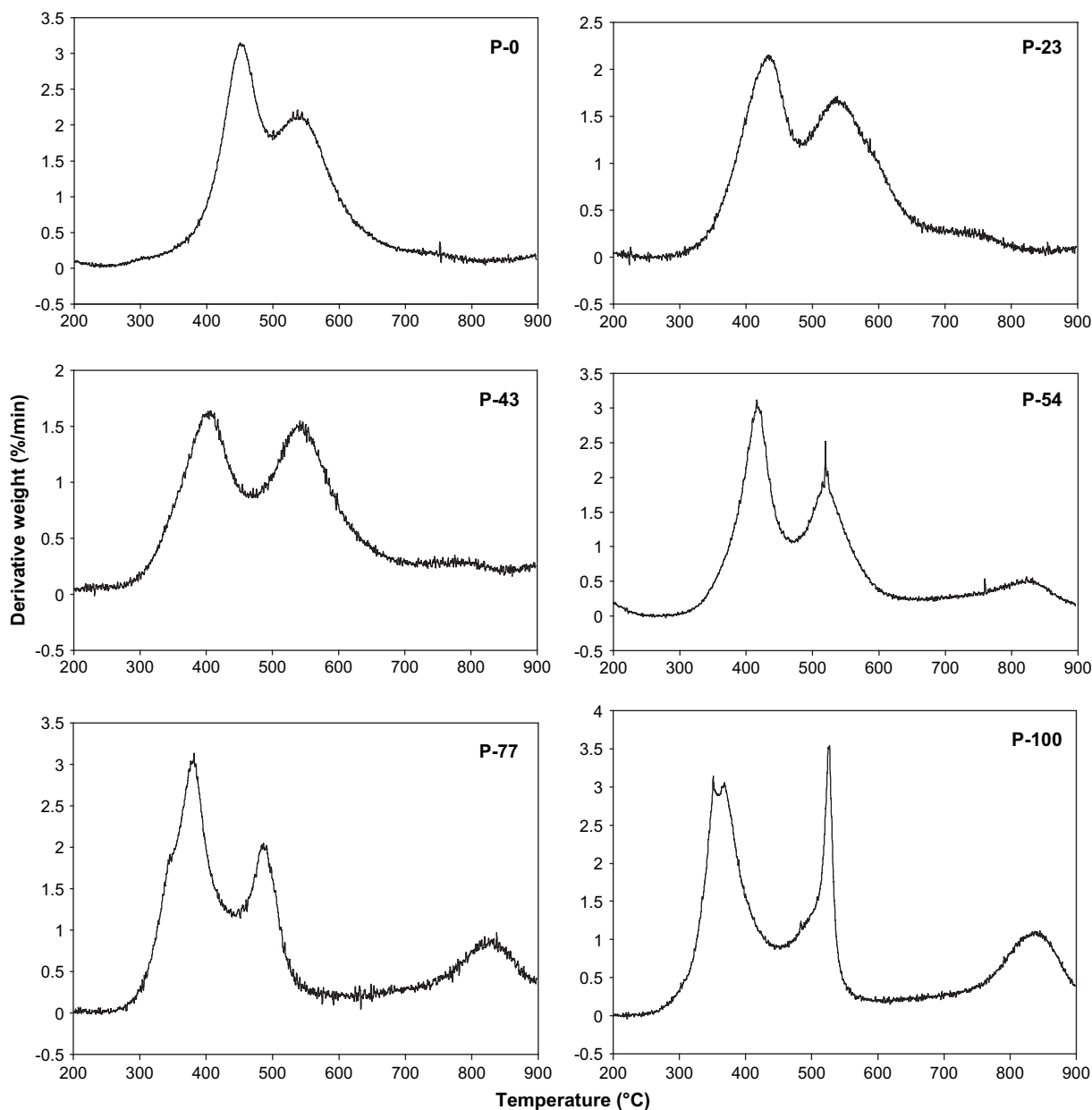


Fig. 3. Derivative thermograms (DTG) of BHDB-polymers under nitrogen atmosphere.

**Table 2**  
Pyrolysis products from BHDB-polyphosphonate (P-100) and polyarylate (P-0)

Entry	Molecular weight	Pyrolysis product	Percent of total area				
			Polyphosphonate		Polyarylate		
			500 °C	650 °C	900 °C	550 °C	800 °C
1	18–44 <sup>a</sup>	H <sub>2</sub> O, CO, and CO <sub>2</sub>	12.3	2.7	9.5	20.7	26.3
2	78	C <sub>6</sub> H <sub>6</sub>	27.8	84.6	81.8	–	9.0
3	94	C <sub>6</sub> H <sub>5</sub> OH	55.3	12.4	6.3	20.7	22.7
4	108	4-MeC <sub>6</sub> H <sub>4</sub> OH	4.5	3.5	0.2	4.8	9.5
5	110	1,2-C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub>	–	–	–	1.6	–
6	122	4-HOC <sub>6</sub> H <sub>4</sub> CHO	–	–	–	3.4	2.7
7	122	C <sub>6</sub> H <sub>5</sub> COOH	–	–	–	14.0	17.7
8	154	C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub>	–	0.2	1.3	–	–
9	198	C <sub>6</sub> H <sub>5</sub> COOC <sub>6</sub> H <sub>5</sub>	–	–	–	–	1.3

<sup>a</sup> Small molecules could not be effectively separated by the GC column that has been employed in the present study.

allow calculation of the full model compounds, recognizing that the resulting bond strengths are valuable as relative rather than absolute values. Comparisons of B3LYP calculations with 6-31+G(d) [20,21] and 6-31G(d,p) [21] basis sets found absolute deviations of 12–27 kJ/mol for a wide variety of molecular architectures. The unrestricted method was used in all the calculations. Each structure was optimized and energy calculated using Gaussian 98 [22].

### 3. Results and discussion

The BHDB-polymers used in this study are depicted in Fig. 1. Their molar compositions, molecular weights, HRCs, char yields, and estimated LOI values (using van Krevelen's numerical method [13]) are given in Table 1. The polymers are denoted by their phosphonate composition "P" (i.e., the homopolyphosphonate is P-100, while the copolymer containing 23 mole percent phosphonate units is P-23).

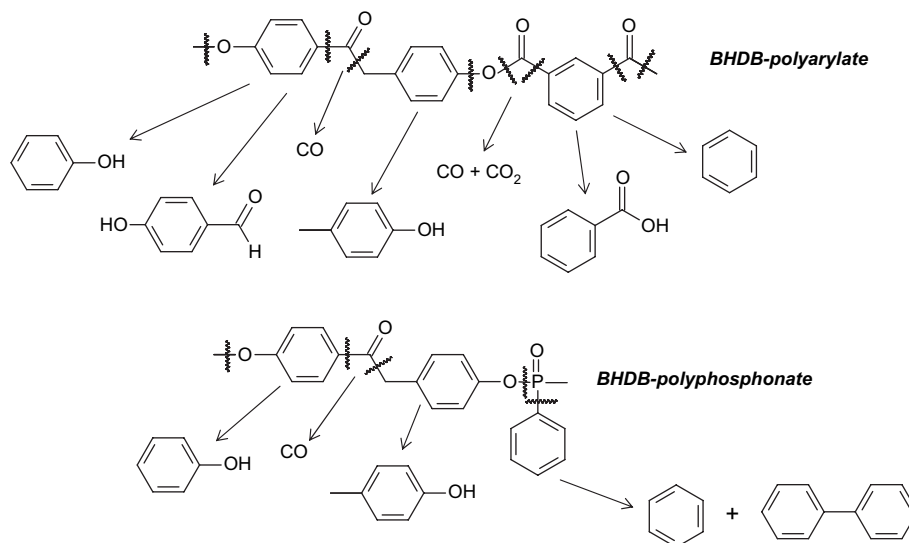


Fig. 4. BHDB-polyarylate and polyphosphonate decomposition products.

### 3.1. Thermogravimetric analysis (TGA)

TGA and derivative thermogravimetry (DTG) were performed on the BHDB-copolymers as a precursor to the Py-GC/MS studies. The BHDB-polymers exhibit high thermal stability, with decomposition temperatures in the 350–400 °C range at 5% weight loss. The presence of phosphorus in the backbone has a profound effect on the thermal decomposition, as reflected in the TGA and DTA profiles of Figs. 2 and 3. The char yields (at 800 °C) for BHDB-polyarylate and polyphosphonate homopolymers were 45 and 52%, respectively, whereas the char yields for the arylate–phosphonate copolymers were in the range of 50–58%. Degradation of deoxybenzoin moieties into char, postulated to go through

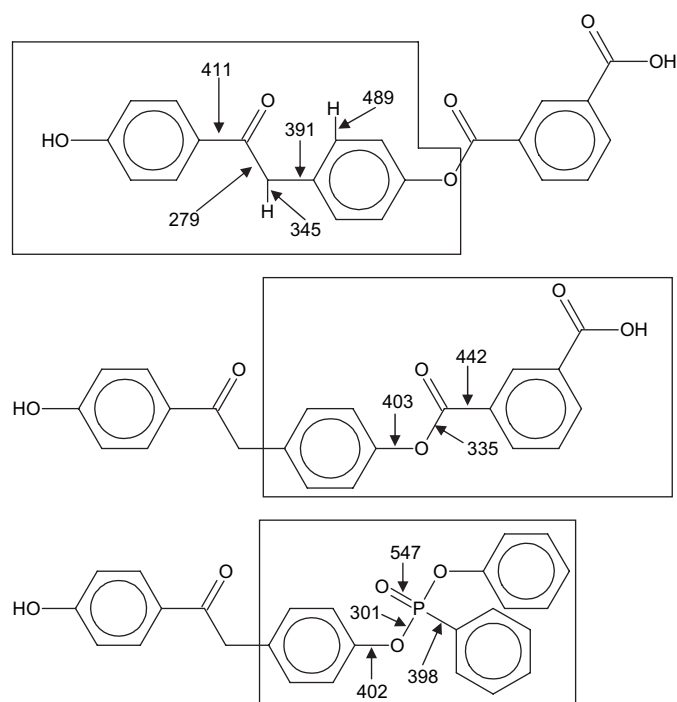


Fig. 5. UB3LYP/6-31G(d) quantum bond energies in kJ/mol for BHDB-polyarylate and polyphosphonate polymer representative structures. Representative structures used for the calculations are shown by the outline.

diphenylacetylene, contributes to the observed high char yields [11]. The replacement of aryates with phosphonates increases the char yield to 52%. In contrast, the incorporation of phosphorus does not induce this type of effect in polymers based on BPA. Replacement of isophthalate by phenylphosphonate in BPA-polyarylate leads to decreased char yield from 30 to 23%.

The higher char of the BHDB-copolymers implies a synergism between the phosphonate, isophthalate and deoxybenzoin groups. Oxygen-rich isophthalate and deoxybenzoin units of the copolymers seem to promote char formation readily in conjunction with the phosphonate units. This effect is in accord with prior work on phosphorus-based flame retardants, in which char formation is promoted more efficiently in oxygen-containing polymers such as polycarbonates [23], polyurethanes [24], polyesters [25], polymethylmethacrylates [26], epoxies [27], and nylon-6 [28]. The thermal degradation of phosphorus compounds with these polymers produces phosphoric acid and polyphosphoric acid, which persists in the condensed phase and catalyzes char formation [29]. The polyphosphoric acid forms a continuous coating over the burning polymer as a barrier to heat and oxygen transport [30]. For an oxygen-free polymer like polystyrene, the acid-catalyzed char-forming action of phosphorus is less pronounced, relying instead on the presence of a separate oxygen-containing molecule [31].

Despite the relatively close HRC values of the BHDB-based polyarylates and polyphosphonates, their thermal decomposition mechanisms are qualitatively different, as seen from the derivative thermograms (DTG) depicted in Fig. 3. BHDB-polyarylate decomposition has two closely associated peaks, with maxima at 450 and 540 °C, while the DTG curve of the polyphosphonate exhibits three distinct peaks, with maxima at 380, 530 and 840 °C. In case of the copolymers, the DTG curves reflected the relative amount of aryate or phosphonate in the structure.

### 3.2. Pyrolysis-gas chromatography/mass spectrometry

Py-GC/MS was employed to analyze the volatile products arising from the decomposition of BHDB-polymers. Using DTG data as a guide, pyrolysis studies were carried out consecutively at the high temperature end of each decomposition step for the BHDB-polymers. In general, increased heating rates postpone decomposition to higher temperatures. Considering the faster heating rate employed in Py-GC/MS (260 °C/min) as compared to the TGA (10 °C/min), the pyrolysis was performed at 500, 650, and 900 °C.

This approach enabled isolation of each decomposition step, so that the volatile products formed in each step (mostly primary products) could be analyzed separately. In a similar manner, the pyrolysis experiments were carried out at 550 and 800 °C for the BHDB-polyarylate (P-O). A summary of the relative peak intensities of the major observed volatile compounds for BHDB-polyphosphonate and polyarylate is presented in Table 2.

The first decomposition step (pyrolysis at 500 °C) of BHDB-polyphosphonate reveals phenol as the major product (55%) followed by benzene (28%). 4-Methylphenol, carbon dioxide, carbon monoxide, and water were also observed. A decomposition pattern of the BHDB-polyphosphonate and resulting decomposition products is postulated in Fig. 4. The relative ratio of decomposition products indicates that this first decomposition step corresponds to the degradation of the deoxybenzoin component (phenol, 4-methylphenol, and benzene) of the polymer, along with the onset of degradation of the phosphonate moiety giving benzene. At the subsequent steps (650 and 900 °C), degradation of phenylphosphonate moieties dominates, as evident from detection of benzene (>80%). Interestingly, phosphorous appears confined exclusively to the condensed phase, as no trace of phosphorus-containing compounds was detected in the volatile products.

The BHDB-polyarylates showed two nearly overlapping decomposition steps. Thus, the volatiles observed during its pyrolysis are expected to be resulting from a simultaneous degradation of both the deoxybenzoin and the isophthalate units. As seen from Table 2, phenol and 4-methylphenol were the main decomposition products obtained from deoxybenzoin part, while isophthalate unit gives rise to benzoic acid, benzene, and small molecules like CO and CO<sub>2</sub> (Fig. 4). The concurrent decomposition of both bisphenolic and

isophthalate moieties of the BHDB-polyarylate was responsible for the presence of considerably large amounts (20–26%) of highly volatile products such as H<sub>2</sub>O, CO, and CO<sub>2</sub>. Formation of water could be accounted for by the dehydration of deoxybenzoin units to diphenylacetylene intermediate, which upon subsequent aromatization would convert into char. Carbon monoxide and carbon dioxide could result from the decarboxylation of the isophthalate unit into benzoic acid and benzene. A small fraction of water formation may also be accounted for by the esterification reaction of the primary volatile products, benzoic acid and phenol to phenyl benzoate.

Quantum mechanical calculations [B3LYP/6-31G(d)] of the bond energies of BHDB-polyarylate and polyphosphonate are shown in Fig. 5 for the deoxybenzoin, isophthalate, and phosphonate components. A base density-functional method and modest basis set [UB3LYP/6-31G(d)] were chosen to allow calculation of the full model compounds recognizing that the resulting bond strengths are valuable as relative rather than absolute values. The weakest bond is carbonyl–methylene C–C bond (279 kJ/mol), which accounts for the formation of initial products 4-hydroxybenzaldehyde and 4-methylphenol. Further fragmentation in the order of bond energies would lead to the formation of phenol, benzoic acid, benzene, etc. that are given in Table 2.

### 3.3. Bisphenol A-containing polyarylate and polyphosphonate

The decomposition of BPA-polymers (polyarylate and polyphosphonate) was then examined by Py-GC/MS for comparative purposes. As seen from the TGA and DTG curves (Fig. 6) both these BPA-polymers show single-step decompositions, indicating

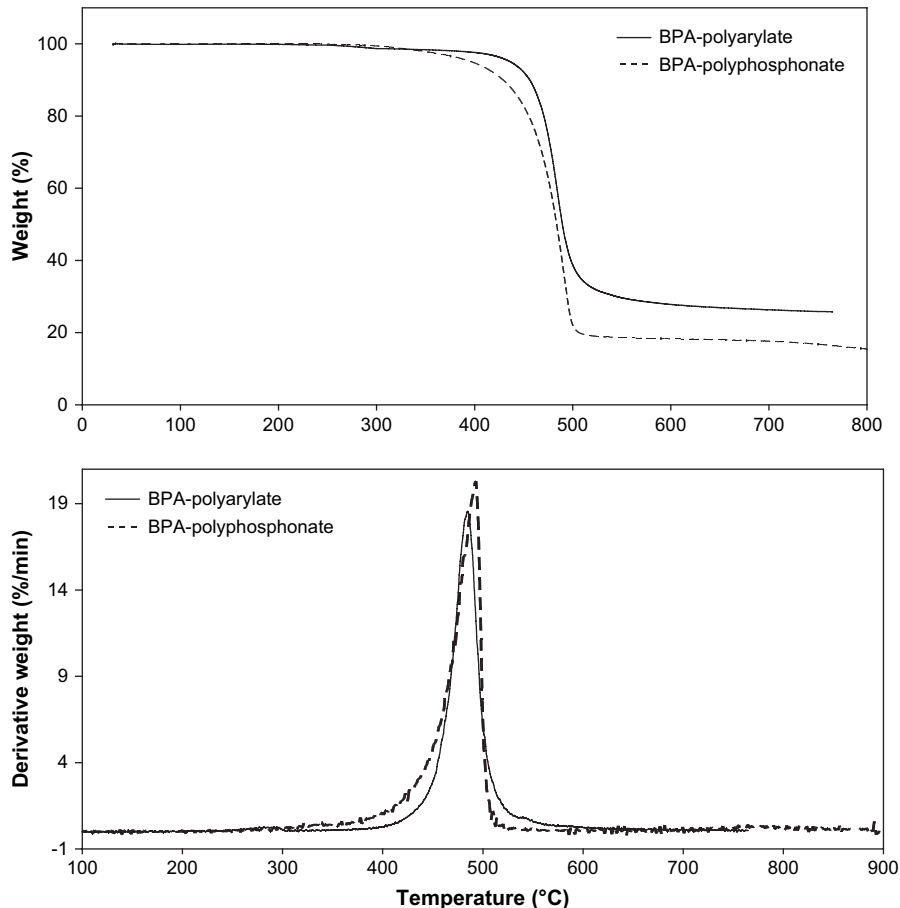


Fig. 6. TGA data for BPA-based polyarylate and polyphosphonate under nitrogen atmosphere.

**Table 3**  
Pyrolysis products from BPA-polyphosphonate and polyarylate

Entry	Molecular weight	Pyrolysis product	Percent of total area			
			Polyphosphonate		Polyarylate	
			550 °C	800 °C	550 °C	800 °C
1	18–44 <sup>a</sup>	H <sub>2</sub> O, CO, and CO <sub>2</sub>	–	–	7.6	1.6
2	94	C <sub>6</sub> H <sub>5</sub> OH	45.5	–	16.0	25.5
3	108	4-MeC <sub>6</sub> H <sub>4</sub> OH	–	–	–	3.7
4	122	C <sub>6</sub> H <sub>5</sub> COOH	–	–	11.0	5.5
5	134	C <sub>6</sub> H <sub>5</sub> CMe <sub>3</sub>	16.1	–	–	–
6	134	4-HOC <sub>6</sub> H <sub>4</sub> C <sub>3</sub> H <sub>5</sub>	–	–	17.0	18.2
7	136	4-HOC <sub>6</sub> H <sub>4</sub> CHMe <sub>2</sub>	3.1	–	–	4.0
8	136	C <sub>6</sub> H <sub>5</sub> COOMe	–	–	7.6	–
9	148	3-MeCOC <sub>6</sub> H <sub>4</sub> CHO	–	–	7.0	–
10	194	1,3-C <sub>6</sub> H <sub>4</sub> (COOMe) <sub>2</sub>	–	–	5.3	–
11	196	C <sub>6</sub> H <sub>5</sub> CMe <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	–	–	–	5.3
12	198	C <sub>6</sub> H <sub>5</sub> COOC <sub>6</sub> H <sub>5</sub>	–	–	–	9.8
13	210	4-MeC <sub>6</sub> H <sub>4</sub> CMe <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	20.1	–	28.4	12.6
14	212	4-HOC <sub>6</sub> H <sub>4</sub> CMe <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	–	21.2	–	–
15	262	Ph <sub>3</sub> P	11.4	58.1	–	–
16	278	Ph <sub>3</sub> PO	–	7.1	–	–

<sup>a</sup> Small molecules could not be effectively separated by the GC column that has been employed in the present study.

a different thermal degradation pathway relative to the BHDB-polymers.

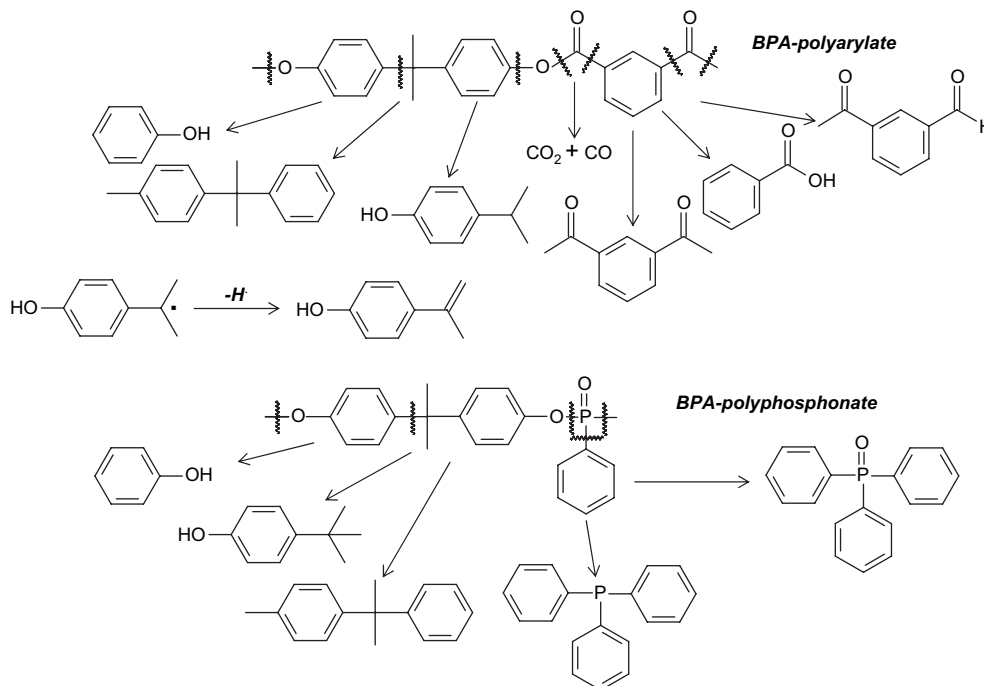
In BPA-polyarylate, the observation of almost equal ratios of the decomposition products from the bisphenol and isophthalate moieties indicates their simultaneous decomposition. For BPA-polyphosphonate, the decomposition at 550 °C yields the majority of products from the bisphenol part (BPA), along with small amounts of phosphorus-containing product (~11%), as depicted in Table 3 and Fig. 7. However, at a higher temperature (800 °C), the majority of the volatile decomposition products arise from the phosphonate. The evolution of phosphorus-containing compounds, triphenylphosphine and triphenylphosphine oxide, in the volatile products accounts for the lower char of BPA-polyphosphonate relative to the corresponding arylate. These observations are in line with the previous reports that phosphorus

promotes char formation, by condensed phase activity, particularly in case of oxygen-rich polymers [23–28].

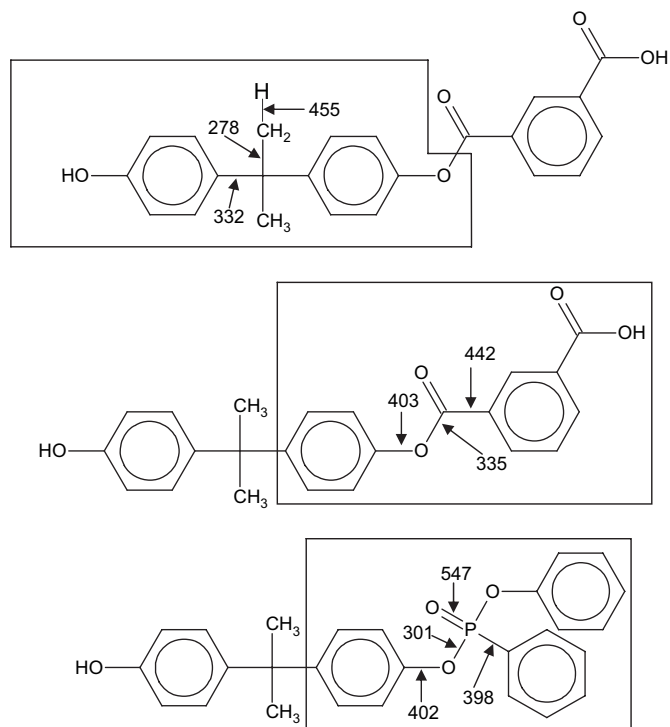
The calculated energies for the BPA-derived polymers are shown in Fig. 8. The relatively low bond energy associated with the quaternary carbon in BPA reflects its facile decomposition. In the case of BPA-polyphosphonates, it appears that the low bond energies allow the BPA portion to pyrolyze, followed by the phosphonate pyrolyzing at 800 °C. The ease of methyl radical evolution also increases the heat release capacity, providing an additional pathway for further decomposition.

#### 3.4. BHDB-poly(arylate-co-phosphonate)s

Py/GC–MS of the BHDB-arylate/phosphonate copolymers (P-54) is given in Table 4. The pyrolysis experiments were carried out



**Fig. 7.** Thermal degradation pathway for BPA-polyarylate and polyphosphonate.



**Fig. 8.** UB3LYP/6-31G(d) quantum bond energies in kJ/mol for BPA-polyarylate and polyphosphonate polymer representative structures. Representative structures used for the calculations are shown by the outline.

at 500, 650 and 900 °C, consecutively. The first step was accompanied by decomposition of deoxybenzoin units (phenol ~40% and 4-methylphenol ~6%) along with onset decomposition for isophthalate and phosphonate moieties (benzoic acid ~2%; benzene ~15%). The second step of pyrolysis, at 650 °C, comprises phosphonate degradation, as indicated by the formation of benzene as the major product (55%), along with the further decomposition of deoxybenzoin and isophthalate units. The pyrolysis products obtained from the deoxybenzoin unit (phenol and 4-methylphenol) decreased at this temperature (~26%) and continued to diminish to ~4% at 850 °C. Benzoic acid (~2%) as a decomposition product of isophthalate moieties was also observed, and degradation of the phosphonate moiety continued into the final step as well. Significant amounts of water and carbon dioxide were observed throughout the decomposition ramp.

#### 4. Conclusions

The thermal decomposition of BHDB-polyarylates, polyphosphonates, and poly(arylate-co-phosphonate)s was analyzed by Py-GC/MS. The thermal degradation of BHDB-polyarylate, under

nitrogen atmosphere, revealed two closely associated steps corresponding to the simultaneous decomposition of deoxybenzoin and isophthalate units. BHDB-polyphosphonate exhibited a three-step decomposition, initialized by degradation of deoxybenzoin units, followed by decomposition of the phenylphosphonate units. The decomposition mechanism of BHDB-copolymers was dictated by the composition of arylate and phosphonate units. The presence of phosphorus induced a synergetic effect with oxygen-rich isophthalate and deoxybenzoin units leading to char yields as high as 58% for the copolymers.

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**Table 4**

Pyrolysis products from BHDB-copolymer (P-54)

Entry	Molecular weight	Product of pyrolysis	Percent of total area		
			500 °C	650 °C	900 °C
1	18–44 <sup>a</sup>	H <sub>2</sub> O, CO, and CO <sub>2</sub>	34.8	15.3	52.5
2	78	C <sub>6</sub> H <sub>6</sub>	15.4	55.2	41
3	94	C <sub>6</sub> H <sub>5</sub> OH	39.3	23.3	4.4
4	108	4-MeC <sub>6</sub> H <sub>4</sub> OH	6.0	2.7	–
5	122	C <sub>6</sub> H <sub>5</sub> COOH	1.7	2.1	–
6	154	C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub>	–	–	1.3

<sup>a</sup> Small molecules could not be effectively separated by the GC column that has been employed in the present study.

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