Thermal decomposition and flammability of fire-resistant, UV/visible-sensitive polyarylates, copolymers and blends

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Abstract

Thermal decomposition behavior and flammability of three polyarylates based on bisphenol A (BPA), 1,1-dichloro-2,2-bis(4-hydroxy-phenylethylene (BPC II) and 4,4'-dihydroxy-3-ethoxy-benzylidenooacetophenone (Chalcon II), their copolymers and blends were investigated by pyrolysis GC/MS, simultaneous thermal analysis and pyrolysis-combustion flow calorimetry (PCFC). The relationships between flammability and structure/composition of these polymers have also been explored. It is found that BPC II-polyarylate is an extremely fire-resistant thermoplastic that can be used as an efficient flame retardant agent to be blended with the other polymers. Chalcon II-polyarylate is of interest as a UV/visible-sensitive polymer with a relatively low heat-release rate and a high char yield. PCFC results show that the total heat of combustion of the copolymers or blends changes linearly with the composition, but the change of maximum heat-release rate and char yield depends greatly on the chemical structure of the components.

Keywords: Polyarylate; Thermal decomposition; Flammability

1. Introduction

With the increasing stringent requirements on the fire safety of materials, searching for new heat- and flame-resistant polymers has attracted considerable research activity during the last 30 years [1–5]. Polyarylates, a group of aromatic polyesters of phthalic acid and bisphenols, represent a very important family of engineering thermoplastics with enhanced long-term resistance to elevated temperature in advanced applications. They have many good properties, such as high modulus, flexural recovery, high heat deflection temperature, low notch sensitivity, and good electrical properties. Most of all, these materials show a high resistance to ignition and flame spreading without additives [6]. A high-temperature wholly aromatic polyester, poly(p-hydroxybenzoic acid), was one of the first developed polyarylates. It is highly crystalline and does not melt below its decomposition temperature (450 °C) [6].

Varying the structures of phthalic acids and bisphenols, a series of polyarylates has been synthesized. Among them, polyarylates based on chloral and its derivatives have been found to be extremely fire-resistant [7]. This result is supported by the discovery of the non-flammable nature of chloral homopolymer and copolymers due to their high chlorine content [8–11]. However, these materials are insoluble and infusible, so they have not found practical application. Nonetheless, because chloral can easily react with different aromatic hydrocarbons, one promising aspect is to use chloral as a starting material for the manufacture of different monomers. Since 1964, many kinds of chloral-based polymers have been studied [7]. Polyarylates based on 1,1-dichloro-2,2-bis(4-hydroxy-phenylethylene (BPC II) have received considerable interest due to their good solubility, mechanical, dielectrical, optical and excellent heat- and flame-resistant properties [12–14]. Brzozowski was one of the first to use BPC-II in the synthesis of polycarbonates and polyarylates through interfacial polycondensation [15–17]. It is found that these polymers are the least combustible and fuming of all existing thermoplastics. Recently, UV/visible-sensitive polyarylates with improved thermal and chemical stability have become his major research topics [18–21]. Chalcon II (4,4'-dihydroxy-3-ethoxy-benzylidenoacetophenone)-polyarylate is of
particular interest due to its high UV-sensitivity, economic (high yield) and ecological (non-toxic) advantages [22,23]. Its copolymers with bisphenol A (BPA) or BPC II monomer meet the main requirements for photoreists (e.g. high UV-sensitivity, high chemical resistance, high adhesion, high tenacity, good solubility in harmless solvents). The images have a very good resolution and contrast and can be easily developed. Therefore, these polarylates are potentially useful for photolithography process and some other photopolymer applications [22].

There are many methods to reduce polymer flammability. Although it is important to develop some brand-new fire-resistant polymers, the simplest way to control flammability from a commercial standpoint is to modify the structure and composition of existing polymers by either copolymerization or polymer blending. These methods can minimize the effects of small-molecule flame-retardant additives on the processing and performance of the host polymers and avert outward diffusion in the system and the consequent risk of environmental contamination. On the other hand, some other properties of the host polymers can also be improved. However, two important issues must be considered when blending. One is the compatibility between polymers. The other is the cost-efficiency of blending a small amount of a very flame-retardant high-charring polymer with a large amount of a very flammable low-charring polymer. Until now, little has been done in the field of flammability–composition relations except for some studies on BPA-, BPC II-polycarbonates [24,25]. However, discovering the intrinsic relationships between polymer structures, composition and their fire behavior can greatly help identify and design new fire-safe polymeric materials.

In order to fully evaluate the fire behavior of different polymers, it is necessary to develop some standard tests for assessing the flammability and other combustion-related properties of polymers. Most countries have standards and codes for the classification of materials with respect to their combustion behavior, but the experimental set-ups used in existing standard tests vary considerably according to the nature, shape and size of the polymeric materials to be tested. The rank order of the fire performance of many virgin polymers has been assessed by some small-scale flammability tests, such as limiting oxygen index and cone calorimetry. However, all these tests still require relatively large samples, and the results are determined not only by the characteristic of the materials involved in fire but also by a multitude of conditions and factors. Thus, it would be a great improvement to establish a relatively low-cost, convenient and quantitative test to set up another evaluation standard. Pyrolysis-combustion flow calorimeter (PCFC) [26–28] is a very new, rapid and quantitative flammability test. It is operated on the oxygen consumption principle; i.e. the net heat of complete combustion of typical organic molecules per mole of oxygen consumed is relatively constant, \( E = 419 \pm 19 \text{ kJ/mol O}_2 = 13.1 \pm 0.6 \text{ kJ/g O}_2 \), which is essentially independent of the chemical compo-

sition of the combusted materials. Using only milligram samples, PCFC is an extremely good method to characterize materials that are only available in a small amount. The 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 the char yield can be directly obtained from PCFC. The correlations between PCFC and some standard tests, such as oxygen bomb calorimeter according to ASTM D2382, cone calorimeter at 50 kW/m\(^2\) incident heat flux according to ASTM E1354, and Underwriter Laboratories Test for Flammability of Plastic Materials (UL-94), are all fairly good [29]. Therefore, PCFC is an efficient screening tool for newly synthesized fire-resistant materials.

In this paper, three major experimental techniques—pyrolysis gas chromatography/mass spectroscopy (PyGC/MS), simultaneous thermal analysis (STA) and pyrolysis-combustion flow microcalorimetry (PCFC)—are used to fully characterize the thermal decomposition and flammability of three polyarylates based on BPA, BPC II and Chalcon II monomers, their copolymers and blends. The relationships between chemical structure/composition and heat/flame resistance of these polyarylates have also been investigated.

2. Experimental

2.1. Synthesis

Polyarylates based on bisphenol A (BPA), 1,1-dichloro-2,2-bis(4-hydroxy-phenyl)ethylene (BPC II) and 4,4'-dihydroxy-3-ethoxy-benzylidenocetophenone (Chalcon II) were synthesized by interfacial polycondensation (Scheme 1). The water phase consisted of bisphenols in an alkali solution and a phase transfer catalyst (PTC), such as cetyltrimethylammonium bromide (CTMA Br). The organic phase (methylene chloride) consisted of an acid chloride mixture (terephthalic and isophthalic acid chloride in a molar ratio of 1:1). The two-phase mixture was stirred at a rate of 2000 rpm for 2 h at room temperature, and then 10% hydrochloric acid was added to obtain pH 1. After 15 min, the phases were separated and the methylene chloride phase with dissolved polymers was poured into strongly stirred methanol. The precipitated polyarylate was filtered and dried at 70 °C under vacuum. Copolymers with various molar fractions of BPA, Chalcon II and BPC II monomers were prepared by the same method. Polymer blends were made by dissolving different polymers with varied weight ratios into methylene chloride, then solution-casting into films.

The polymers used for blending are as follows: polysulfone (–O–Ph–C(CH\(_3\))\(_2\)–Ph–O–Ph–SO\(_2\)–Ph–) was supplied by BP Amoco Co.; polystyrene (\(M_p = 514\,000\)) was obtained from Polymer Laboratories; and
poly(ethylene oxide) ($M_n = 600,000$) was purchased from Aldrich.

### 2.2. Characterization

Differential scanning calorimetric (DSC) measurements were carried out on a DuPont 2910 instrument. Thermal stability was examined by a TA Instrument 2050 thermogravimetric analyzer (TGA). Simultaneous thermal analysis (STA = TGA/DSC) was performed with Rheometric STA 1500 to study the heat evolved or absorbed during thermal decomposition. Char yield for the polymers has been defined as the amount of solid residue at 930 °C.

The sample weight for all the thermal analyses was approximately 10 mg, the heating rate was 10 °C/min and the experiments were performed under N₂.

Flammability of the polymers was measured by the PCFC [26–28]. Sample weight was 1.0 ± 0.1 mg and the interface temperature was maintained just below the onset decomposition temperature. Samples were pyrolyzed at 930 °C at 4.3 °C/s in N₂ and then completely combusted at 900 °C. The results were the average of five measurements for each sample.

The decomposition products were characterized by pyrolysis GC/MS. About 0.1–0.2 mg of samples were pyrolyzed in a commercial device (Pyroprobe 1000/2000) to 930 °C at a heating rate of 4.3 °C/s (the same pyrolysis conditions as in PCFC measurements). Volatiles from pyrolysis were separated by a Hewlett Packard 5890 series II gas chromatograph (GC) and analyzed with a Hewlett Packard 5972 series MS spectrometer. The column was a HP fused-silica capillary column (crosslinked 5% PH ME siloxane, 0.25 mm in diameter and 30 m long). Oven temperature was programmed from 36 to 295 °C at a heating rate of 10 °C/min and then held at 295 °C for about 15 min. The mass range scanned was from m/z 11 to 550.

UV/visible spectra were recorded by using a HP 8453 UV/visible spectrophotometer. The cured samples used for TGA and PCFC analyses were prepared under an OAI 500 W deep-UV lamp with intensity of 10 mW/cm².

### 3. Results and discussion

#### 3.1. Effects of phase transfer catalysts on the flammability and thermal properties of BPA-polyarylates

Three kinds of PTCs—cetyltrimethylammonium bromide (CTMA Br), crown ether (18-crown-6) and dimethyl sulfoxide (DMSO)—have been used to optimize the interfacial polymerization conditions of BPA-polyarylate. It has been found that the polymers obtained by using 18-crown-6 and DMSO have higher molecular weight, thus higher glass transition temperature ($T_g$) and higher thermal stability (Table 1).

The flammability of all the polymers is measured with PCFC developed by Lyon and Walters [26–28]. Heat release rate (the most important parameter for evaluating polymer flammability) is calculated from the measured oxygen consumption. Heat release (HR) capacity, which depends only on the chemical composition of the solid, is obtained by dividing maximum heat release rate by the sample weight and heating rate. It is a reliable measure of the fire hazard of a material. Direct integration of the heat release rate versus time gives the total heat of combustion of the fuel gases per unit sample mass. Char yield is determined by weighing the sample before and after the test. It can be seen from Table 1 that the increase of molecular weight has no significant effect on the flammability of BPA-polyarylate due to its random-scission decomposition mechanism.

#### 3.2. Thermal decomposition and flammability of homopolymers

Thermal decomposition processes of BPA-, Chalcon II- and BPC II-homopolyarylates are shown in Fig. 1. It can be seen that all the polymers decompose in a single step. They all have a relatively high thermal stability and will not start to lose weight dramatically until 370 °C. However, the bridging groups and side groups in the bisphenols do have some effects on the heat resistance of polyarylates. The introduction of 1,1-dichloroethylene groups (BPC II) leads to an obvious drop (40 °C) in thermal stability when
compared to BPA-polyarylate. The thermal stability of Chalcon II-polyarylate is also greatly reduced due to the presence of bulky ethoxy side groups. The order of the thermal stability of these homopolyarylates (according to the onset decomposition temperatures) is BPA (450 °C) > BPC II (414 °C) > Chalcon II (390 °C). From the derivative of TGA curves (DTG curves), we can see that the mass loss rate of BPC II- and Chalcon II-polyarylates are significantly lower than that of BPA-polyarylate, which indicates that BPC II- and Chalcon II-polyarylates decompose much slower. Moreover, these two polymers can produce more char at high temperatures (above 40%).

The heat events involved in the thermal decomposition are characterized by STA, which can perform TGA and DSC simultaneously up to 1200 °C. The high-temperature DSC curves are shown in Fig. 2. It can be seen that all the polymers are amorphous, with $T_g$S around 140–150 °C and onset decomposition temperatures around 400 °C. The large temperature window between softening and thermal decomposition allows processing by injection and extrusion molding. During decomposition, BPA- and Chalcon II-polyarylates show an endothermic peak, but BPC II-polyarylate decomposes exothermically, which might be due to the formation of HCl or some special charring processes.

Table 2 shows the PCFC results as well as some TGA results, from which we can see that different bridging groups in bisphenols have also a large influence on the flammability of polymers. Generally, the flammability of polymers is determined by many factors, of which rate of decomposition (mass loss rate) and the amount and flammability of volatiles produced are the most important. The introduction of crosslinking groups (double bond in Chalcon II and BPC II) can greatly enhance the formation of char and therefore reduce the amount of fuel generated. According to the pyrolysis GC/MS analyses (Fig. 3), the major decomposition products of BPA- and Chalcon II-polyarylates are a series of phenols and some other flammable aromatic compounds. However, BPC II-polyarylate gives out relatively less of flammable compounds (such as phenols), but more CO$_2$, CO, HCl and some chlorinated aromatic compounds which have relative low fuel values and may also confer flame-retardant effects in the gas phase. Therefore, the reduced flammability of Chalcon II-polyarylate (compared with BPA-polyarylate) is mainly due to low mass loss rate and less amount of fuels generated. While in the case of BPC II-polyarylate, release of less flammable decomposition products is another important factor for its low flammability. In all, compared with some other commercial polymers, Chalcon II- and BPC II-polyarylates are more heat- and flame-resistant, and BPC II-polyarylate has especially low flammability.

### 3.3. UV/visible-sensitive Chalcon II-polyarylate

Chalcon II-polyarylate is a UV/visible-sensitive polymer containing –CH=CHC(O)– groups. The UV spectra of
Chalcon II-homopolymer and copolymers are shown in Fig. 4. Besides the peak at 238 nm which can be attributed to the absorption of phenyl ring, there is another broad absorption between 300 and 400 nm which is due to the \(-CH=CHC(O)–\) structure. For the copolymers, with the increased content of Chalcon II-monomer, the intensity of that absorption increases accordingly.

It had been reported that some UV-sensitive polyarylates

![UV spectra of polyarylates containing Chalcon II-monomer](image)

Fig. 4. UV spectra of polyarylates containing Chalcon II-monomer. (a) Homopolymers and (b) BPA–Chalcon II copolymers.
with similar structure can form photo-crosslinking after UV exposure [21]. In our studies, in order to know whether photo-crosslinking has an effect on the thermal decomposition and flammability of the polymers, Chalcon II-polyarylate has been exposed to UV or visible light for varied time. It is found that after exposure, Chalcon II-polymer is no longer soluble in methylene chloride, which suggests the formation of photo-crosslinks (Scheme 2).

TGA results show that the thermal stability of the cured polymers is decreased. They start to decompose around 200–250 °C and then merge into the major decomposition step after about 6% weight loss (Fig. 5). The decrease in thermal stability is apparently due to disruption of the conjugated system and the formation of weak linkages around crosslinking points (Scheme 2).

It is also found that the TGA curves of polymers cured for more than 4 min are almost overlapped with each other, which means the photo-curing process is completed after 4 min. This conclusion is confirmed by other studies [21,22] that also show that the mechanical properties of the polymers can be greatly improved by curing. However, the flammability measured by the PCFC method shows no difference between cured and non-cured samples.

Fig. 5. Thermal decomposition of Chalcon II-polyarylate after UV/visible-exposure. (a) Full TGA curves and (b) initial decomposition.

Fig. 6. Thermal properties of Chalcon II–BPC II copolymers. (a) TGA and (b) DSC (the numbers are molar ratios).
3.4. Thermal decomposition and flammability of copolymers and terpolymers

Thermal decomposition and flammability of three series of copolymers (BPA–Chalcon II, BPA–BPC II, and BPC II–Chalcon II) and BPA–Chalcon II–BPC II terpolymers have been investigated. The results are shown in Figs. 6 and 7 and Table 3.

It can be seen that the thermal decomposition and flammability of copolymers and terpolymers change systematically with composition. With an increased fraction of flame-retardant high-charring units such as Chalcon II or BPC II, the heat release rate and the total heat released are reduced, and the char yield increases correspondingly (Table 3). At a very high concentration of BPC II-monomer (67 mol%), the flammability of the copolymers and terpolymers is completely dominated by the amount of BPC II-units and independent of the structure of the other component, which indicates that BPC II is an efficient flame-retardant comonomer. In addition, the heat involved in the decomposition process changes from endothermic to exothermic with the increased mole fraction of BPC II-units.

After careful investigation on the relationship between flammability and composition (Fig. 8), we found that the total heat released usually changes linearly with the composition. However, the change of HR capacity depends on the chemical structure of the components. For BPA–BPC II and BPA–Chalcon II copolymers, there is an obvious synergistic effect.

3.5. Thermal decomposition and flammability of blends

Four kinds of blends were studied, all of which use BPC II-polyarylate as the flame-retardant component. The choice

![Graph showing thermal properties of BPA–Chalcon II–BPC II terpolymers](image)

**Table 3**

<table>
<thead>
<tr>
<th>Composition (mol ratio)</th>
<th>HR capacity a (J/g K)</th>
<th>Total heat a (kJ/g)</th>
<th>Char a (%)</th>
<th>$T_{max}$ b (°C)</th>
<th>Peak mass loss rate (× 10³/s)</th>
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<td>521</td>
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<td>49</td>
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</table>

a PCFC results.

b Temperature at peak mass loss rate obtained from derivative of TGA curves (DTG).
of the other polymer [polysulfone (PSF), BPA-polyarylate, polystyrene (PS), poly(ethylene oxide) (PEO)] is based on the structure of the polymer and whether this polymer is charring. Several interesting phenomena have been observed regarding thermal stability and flammability. It is found that the thermal stability, decomposition process and char yield of PSF/BPC II-polyarylate blends change systematically with composition (Fig. 9), and the trend of change is similar to BPA-/BPC II-polyarylate blends [30].

However, blends containing PS or PEO behave completely differently during decomposition (Fig. 10). The onset decomposition temperatures of PS/BPC II-polyarylate blends are all the same (around 370 °C, just between the two homopolymers’) regardless of the composition, while the PEO/BPC II-polyarylate blends start to decompose at the same temperature as PEO homopolymer.

As to the flammability, similar to copolymers, the total heat of combustion of blends changes linearly with composition, but the change of HR capacity and char yield is also determined by the type of the other component (Fig. 11). For the blends containing PSF or BPA-polyarylate, the HR capacity and char yield change synergistically.

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Fig. 8. Composition and flammability relationship of copolymers. (a) HR capacity; (b) total heat released: (1) BPA–Chalcon II, (2) BPA–BPC II, and (3) Chalcon II–BPC II.

Fig. 9. TGA curves of PSF/BPC II-polyarylate blends.

Fig. 10. TGA curves of PS (PEO)/BPC II-polyarylate blends. (a) PS/BPC II-polyarylate and (b) PEO/BPC II-polyarylate.
with composition. However, for PS or PEO, they change almost linearly. This is because PS (or PEO) and BPC II-polyarylate are largely phase-separated in the blends due to their distinctive structure difference. Therefore, there is no interaction between these two components during decomposition. However, PSF and BPA-polyarylate have similar aromatic structures to BPC II-polyarylate, and they all can form a certain amount of char on their own. These properties can lead to some kind of intermolecular interaction between two components, which can favor char formation and further slow down the decomposition process. In fact, the decrease in the heat release rate of blends is mainly attributed to the wider decomposition range and therefore lower mass loss rate.

4. Conclusions

BPC II-polyarylate is an extremely heat- and flame-resistant thermoplastic. It can produce about 50% char up to 930 °C. Chalcon II-polyarylate has also very low heat release rate and high char yield. It can be cured under UV/visible light, but the photo-crosslinking formed has no effect on the flammability. The thermal decomposition and flammability of copolymers/terpolymers and blends change systematically with composition. The introduction of a non-flammable high-charring component (BPC II-arylate units) can conveniently control the flame retardance of these polymers. The total heat of combustion of the copolymers/terpolymers and blends changes linearly with composition. However, the change of peak value of heat release rate and char yield greatly depends on the chemical structures of the components.

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