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# Deoxybenzoin-containing polysulfones and polysulfoxides: Synthesis and thermal properties



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# A R T I C L E I N F O

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# ABSTRACT

Novel poly(arylene ether) sulfones, sulfoxides, and sulfides containing deoxybenzoin subunits were synthesized by step growth polymerization involving bishydroxydeoxybenzoin (BHDB) and the corresponding sulfur-containing monomers. The isolated polymers demonstrated good solubility in organic solvents, making them easily processible into transparent, flexible, and creasable films upon solution casting. All of the polymers prepared exhibited exceptionally low flammability characteristics, with total heat release (THR) values as low as 6 J/g-K, and char yield values as high as 54%. Inclusion of deoxybenzoin monomers into polysulfones with 4,4'-biphenyl led to heat release capacity (HRC) values less than half that of commercial polysulfones in use today, placing deoxybenzoin-based polysulfones and polysulfoxides into the ultra-low flammability category.

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#### 1. Introduction

Polymer flammability represents a pressing and persistent societal problem of growing importance with increasing global polymer production, consumption, and waste accumulation [1]. The abundance of synthetic polymers in construction, and transportation vehicles places safety concerns, such as flammability, at a high priority. Efforts to overcome the inherent flammability of high volume polymer materials, as well as specialty products, can improve the safety of polymers and reduce the frequency of firerelated catastrophic events [2].

Many large volume synthetic polymers are highly flammable, such as polyethylene, polystyrene, and poly(methyl methacrylate). Polymers with well-recognized intrinsically low flammability, such as Teflon and Kevlar, cannot nearly cover the range of materials applications for which polymer flammability is problematic. Thus, flame retardant additives, such as halogenated compounds and inorganic fillers, are employed in many finished polymer products. However, some additives carry drawbacks, ranging from toxicity to weakening of mechanical properties and diminished materials performance. New polymers are thus needed that, ideally, satisfy

\* Corresponding author. E-mail address: tsemrick@mail.pse.umass.edu (T. Emrick). both materials performance and flammability requirements simultaneously, without the need for additives of any sort. At the same time, new non-halogenated polymeric additives that reduce the flammability of commodity polymers without sacrificing performance are also desirable. Each approach represents a significant challenge that, if met successfully, will contribute towards improved polymer materials safety.

Recent efforts to reduce the flammability of polymer materials range from new polymer syntheses, to additives and blends, to novel approaches in coating methodology. For example, Grunlan described environmentally friendly anti-flammable nanocoatings for textiles using coating techniques on foam that lead to pore blockage, while fibers coated with a clay-filled flame-retardant film retained their desired flexibility [3]. Morgan reported the synthesis and flammability evaluation of new boron- and phosphonatecontaining aromatic flame retardant polymers produced by metal-catalyzed coupling, and found that adding boronic or phosphonic acids significantly lowered the heat release of the materials as a result of a condensed phase charring mechanism. [4-6]] These polymers were blended with thermoplastic polyurethanes and evaluated by microscale combustion calorimetry (MCC) to afford low heat release polyurethane, with the boronic acids giving optimum performance. Wilkie showed that additives such as ammonium sulfamate, sodium diphenylamine-4-sulfonate, and 3-(1pyridino)-1-propane sulfonate exhibited flame retardant effects





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on both polystyrene and poly(methyl methacrylate).[[7]] In another approach, reduction of polyurethane foam flammability was achieved by carbon nanofiber (CNF) network formation, in which the network reduces dripping of melted material, and lowers heat release values. [8] Gilman described polymer nanocomposites based on nanoclav particles and the formation of a continuous protective solid carbonaceous laver following burning. [9,10]] while Shen employed borates as flame retardants and smoke suppressants in both halogen-containing and halogen-free polymers.[ [11–13]] Fire-resistant intumescent coatings protect a range of materials including wood, textiles and polymer composites, such as acrylic paints with inorganic flame retardant coating compositions. [14] In other approaches, nanoparticles and layer-by-layer (LbL) coatings were applied to the outer layers of thermosets for fire protection, [15–19] with the LbL approach on fabrics, foams, and thin films imparting dramatic improvements in anti-drip behaviour and char formation, while inhibiting flame spread. [20] The distinction of the approach we describe in this manuscript is seen in char-forming ability of deoxybenzoin-based structures, despite its hydrocarbon composition.

The selection of deoxybenzoin moieties for the preparation of low flammability polymers stems from their propensity to undergo substantive char formation upon burning, thus limiting the escape of flammable gas as a source of fuel. [21–23] The deoxybenzoin structure is set up for dehydration at high temperature - under flash vacuum pyrolysis conditions diphenylacetylenes were noted to form from deoxybenzoin precursors. [24-26] Such a functional group transformation in the solid/melt state of a fire would produce polymeric phenylene ethynylenes that should quickly aromatize. cross-link, and char. With respect to characterizing polymer flammability, doing so on an experimental (milligram) scale is extremely useful for probing the potential suitability of novel polymers prior to scale-up efforts. For example, microscale combustion calorimetry (MCC), an oxygen consumption technique, identifies the heat release capacity (HRC) and total heat release (THR) of polymers, both key parameters for predicting polymer flammability in large scale tests, such as the widely implemented UL-94 test. [27–29] The bisphenol of deoxybenzoin, termed bishydroxydeoxybenzoin (BHDB), has now been integrated into several polymer compositions, including polyesters, polyurethanes and epoxy networks, [21,30–32] each giving materials with distinctly low HRC and THR values, while a BHDB-containing polyester was characterized as having a 5 VA rating in the UL94 test, indicative of a very low flammability possessed by a material under these test conditions.

High performance polymers such as polyetherketone (PEK) and polyethersulfone are known for their thermal stability and flame resistant properties. [33,34] Nonetheless, with increasingly rigorous flammability standards, [35–37] we wanted to examine whether the properties of such polymers could be improved further by integrating deoxybenzoin moieties into these structures. This would require compatible polymerization chemistry of the deoxybenzoin monomers with the selected sulfur-containing monomers, such as nucleophilic displacement chemistry performed on the corresponding aromatic difluorides. Examples of polymers that proved amenable to inclusion of deoxybenzoin in the structure are described in this manuscript, as shown in Fig. 1 for deoxybenzoin-containing sulfones **1**, sulfoxides **2**, and sulfone/sulfide copolymers **3**.

# 2. Experimental

# 2.1. Materials

BHDB was prepared from desoxyanisoin [38] and purified by

recrystallization from acetic acid. Desoxyanisoin, pyridine hydrochloride, bis(4-fluorophenyl)sulfone (99%), potassium carbonate, 4,4'-thiodiphenol (99%), thionyl chloride and aluminium chloride were purchased from Sigma—Aldrich. 4,4'-Biphenol (purity > 99.0%) was purchased from TCI and used as received. Sulfolane and fluorobenzene were distilled under vacuum prior to use. Bis(4-fluorophenyl)sulfoxide was synthesized as reported [42] and purified twice by recrystallization from hexane.

# 2.2. Characterization

Monomer syntheses were monitored by thin layer chromatography (TLC) and high performance liquid chromatography (HPLC) eluting with methanol and utilizing UV-detection at 254 nm. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker DPX300 spectrometer. Thermogravimetric analysis (TGA) was performed on a Q500 machine (TA Instruments) at a heating rate of 20 °C/min under  $N_{2(g)}$  atmosphere (flow rate of 200 mL/min), and TGA values are reported as the temperature at which 5% weight loss was observed (T<sub>d</sub>). Polymer glass transition temperature (T<sub>g</sub>) was determined by differential scanning calorimetry (DSC) on a Q200 machine (TA Instruments) with a heating rate of 10 °C/min under  $N_{2(g)}$  atmosphere. Specific heat release rate (HRR, W/g), heat release capacity (HRC, J/(g-K)), and total heat release (THR, kJ/g) were measured on a microscale combustion calorimeter (MCC). MCC was conducted over a temperature range of 80–750 °C at a heating rate of 1 °C/s in an 80 cm<sup>3</sup>/min stream of nitrogen. The anaerobic thermal degradation products in the nitrogen gas stream mix with a 20  $\text{cm}^3$ /min stream of oxygen prior to entering the combustion furnace (900 °C). Heat release is quantified by standard oxygen consumption, [39,40] and HRR is obtained from dQ/dt at each time interval and from the sample mass employed (5 mg). HRC is obtained by dividing the maximum HRR by the heating rate. Polymer molecular weight was measured by gel permeation chromatography (GPC) in DMF with 0.01 M LiCl at 50 °C and calibrated against poly(methyl methacrylate) (PMMA) standards. GPC was operated at an eluent flow rate of 1 mL/min with a Sonntek K-501 pump, one 50  $\times$  7.5 mm PL gel mixed guard column, one 300  $\times$  7.5 mm PL gel 5  $\mu m$  mixed C column, one 300  $\times$  7.5 mm PL gel 5  $\mu m$  mixed D column, and using a Knauer refractive index detector (K-2301) and an Alltech model 3000 solvent recycler.

#### 2.3. Synthesis of 4,4'-bishydroxydeoxybenzoin 4 (BHDB)

BHDB was prepared according to a published procedure.[38] In short, desoxyanisoin (100 g, 390 mmol) and pyridine hydrochloride (180 g, 1.56 mol) were added to a round bottom flask equipped with a condenser and magnetic stir bar. The mixture was refluxed at 200 °C for 5 h, cooled to room temperature, poured into cold water, filtered, and crystallized from acetic acid to afford BHDB as an off-white crystalline solid (76 g, 85%), mp 210–212 °C. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz):  $\delta$  10.35 (s, 1H, OH- Ar–CO), 9.28 (s, 1H, OH-Ar–CH<sub>2</sub>), 7.91 (d, 2H), 8.7 (Ar–H), 7.04 (d, 2H), 8.5 (Ar–H), 6.84 (d, 2H), 8.7 (Ar–H), 6.68 (d, 2H), 8.5 (Ar–H), 4.11 ppm (s, 2H, Ar–CO–CH2–Ar). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>):  $\delta$  196.5, 162.3, 156.2, 131.3, 130.7, 128.1, 125.9, 115.5, 115.4, 43.7 ppm.

#### 2.4. Synthesis of polysulfone 1

To a 100 mL three-necked, roundbottom flask equipped with a Dean Stark trap, condenser, magnetic stirrer, and nitrogen inlet was added BHDB (2.280 g, 10 mmol), bis(4-fluorophenyl)sulfone (2.60 g, 10.2 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (1.40 g, 10.2 mmol), sulfolane (9.5 g), and toluene (10 mL). The mixture was heated to remove water from toluene by azeotropic distillation. The resulting mixture was stirred



Fig. 1. Chemical structures of deoxybenzoin-containing polymeric sulfones 1, sulfoxides 2, and sulfone/sulfide copolymers 3.

at 160–180 °C for 2–3 h. When the mixture became too viscous to allow stirring, an additional 2-3 g of sulfolane was added, and stirring was continued at 180 °C for 30 min. The mixture was cooled to room temperature and diluted with dichloromethane. This solution was poured into methanol (300 mL) containing acetic acid (2 mL), which resulted in precipitation. The precipitated polymer was collected by filtration and redissolved in dichloromethane, and the solution was filtered through a thin layer of Celite to remove inorganic salts. This solution was added to methanol for precipitation. Polymer 1 was collected by filtration and dried under vacuum at 80 °C for 24 h to afford a white fibrous material (4.20 g, 95% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 4.29 (s, 2H, Ar–CO–CH2-Ar), 7.00-7.40 (m, 8H, Ar-H), 7.28-7.30 (d, 2H, Ar-H), 7.84-7.97 (m, 4H, Ar-H), 8.05 (d, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 44.41, 115.56, 117.84, 119.34, 120.54, 130.09, 131.09, 132.629, 135.45, 136.72, 153.87, 155.06, 159.44, 160.28, 161.85, 195.98 ppm. FT-IR (cm<sup>-1</sup>): 3078, 1677, 1579, 1486, 1408, 1291, 1234, 1102, 1009, 993, 871, 832, 685. M<sub>n</sub> 18400, M<sub>w</sub> 57000, PDI 3.1.

#### 2.5. Synthesis of polysulfoxide 2

To a 25 mL three-necked, roundbottom flask equipped with a Dean Stark trap, condenser, magnetic stirrer, and N<sub>2(g)</sub> inlet was added BHDB (1.14 g, 5.00 mmol), bis(4-fluorophenyl)sulfoxide (1.19 g, 5.00 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (0.71 g, 5.2 mmol), sulfolane (4.5 g), and toluene (5 mL). The mixture was heated to remove water (from toluene) by azeotropic distillation. The resulting mixture was heated at 170-180 °C for 15 h. When the mixture became viscous it was cooled to room temperature and diluted with dichloromethane. This solution was poured into methanol (200 mL) containing acetic acid (2 mL), which resulted in precipitation. The precipitated polymer was collected by filtration and redissolved in dichloromethane, and the solution was filtered through a thin layer of Celite to remove inorganic salts. The polymer was purified further by precipitation into methanol. Polymer 2 was collected by filtration and dried under vacuum at 80 °C for 24 h to afford white fibrous polymer. (1.72 g, 80.6% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): 4.27 (s, 2H, Ar-CO-CH2-Ar), 6.90-7.26 (m, 10H, Ar-H), 7.56-7.69 (m, 4H), 8.03-8.06 (d, 2H, Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 44.50, 116.85, 118.22, 120.14, 127.09, 131.03, 138.71, 140.56, 154.61, 158.21, 160.53, 195.99 ppm. FT-IR (cm<sup>-1</sup>): 3060, 1675, 1597, 1504, 1483, 1087, 1041, 871, 829. Mn 13400, Mw 43500, PDI 3.2.

#### 2.6. Representative synthesis of copolymer 9

To a 25 mL three-necked, roundbottom flask equipped with a Dean Stark trap, condenser, magnetic stirrer, and nitrogen inlet was added BHDB (0.570 g, 2.50 mmol), 4,4'-biphenol (0.465 g, 2.50 mmol), bis(4-fluorophenyl)sulfone (1.270 g, 5.00 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (0.72 g, 5.2 mmol), sulfolane (4.2 g), and toluene (5 mL). The mixture was heated to remove water from toluene by azeotropic distillation and stirred at 160–180 °C for 3–4 h. When the mixture became too viscous to stir, an additional 2 g of sulfolane

was added, and stirring was continued at 180 °C for 30 min. The mixture was then cooled to room temperature and diluted with dichloromethane. This solution was poured into methanol (200 mL) containing acetic acid (2 mL), which resulted in precipitation of the polymer. The precipitated polymer was collected by filtration and redissolved in dichloromethane. The dichloromethane solution was filtered through a thin layer of Celite to remove inorganic salts, and the polymer was purified further by precipitation into methanol. Polymer **9** was collected by filtration and dried under vacuum at 80 °C for 24 h to afford white fibrous polymer (2.0 g, 95% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  4.30 (s, 2H, Ar–CO–CH<sub>2</sub>-Ar), 7.12–7.29 (m, 19H), 7.60 (s, 4H), 7.92–8.01 (m, 10H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  44.52 (CH2–CO), 117–120, 129–137, 153–154, 159–161, 196. FT-IR (cm<sup>-1</sup>): 3068, 1678, 1582, 1484, 292, 1233, 1163, 1103, 1007, 830, 686. M<sub>n</sub> 34000, M<sub>w</sub> 64000, PDI 1.9.

#### 2.7. Representative synthesis of copolymer 10

To a 25 mL three-neck round bottom flask equipped with a Dean Stark trap, condenser, magnetic stirrer, and  $N_{2(g)}$  inlet was added BHDB (0.570 g, 2.5 mmol), 4,4'-thiodiphenol (0.545 g, 2.50 mmol), bis(4-fluorophenyl)sulfone (1.271 g, 5.00 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (0.76 g, 5.5 mmol), sulfolane (4.5 g), and toluene (5 mL). The mixture was heated to remove water from toluene by azeotropic distillation, then heated at 160-180 °C for 2-3 h. When the mixture became too viscous to stir, an additional 2 g of sulfolane was added, and stirring was continued at 180 °C for 30 min. The mixture was then cooled to room temperature and diluted with dichloromethane. This solution was poured into methanol (200 mL) containing acetic acid (2 mL), which resulted in precipitation. The precipitated polymer was collected by filtration and redissolved in dichloromethane, and this solution was filtered through a thin layer of Celite to remove inorganic salts. The polymer was purified further by precipitation into methanol, then collected by filtration and dried under vacuum at 80 °C for 24 h to afford a white fibrous material (2.01 g, 92% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 4.33 (s, 2H, Ar-CO-CH2-Ar), 7.01-7.13 (m, 16H, Ar-H), 7.28-7.31 (d, 2H, J = 12), 7.36–7.38 (d, 4H, J = 8), 7.85–7.95 (m, 8H, Ar–H), 8.06–8.08 (d, 2H, J = 8). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 45.50, 119.30, 120.66, 121.97, 131.33, 132.84, 134.45, 136.58, 155.38, 161.24, 163.50, 197.30 ppm. FT-IR (cm<sup>-1</sup>): 3078, 1678, 1578, 1481, 1233, 1175, 1103, 1009, 829, 691. Mn 48,100; Mw 128,000; PDI 2.6.

#### 3. Results and discussion

4,4'-Bishydroxydeoxybenzoin (BHDB), prepared readily by demethylation of desoxyanisoin in neat pyridine hydrochloride,[38] was utilized in step growth polymerization with sulfurcontaining aromatic monomers. Scheme 1 shows the polymerization of BHDB with the selected sulfur-containing aromatic difluorides, accomplished by nucleophilic aromatic substitution in aprotic solvents using potassium carbonate as base and sulfolane as a stable, high boiling solvent.



Scheme 1. Polycondensation of BHDB with difluoroaromatic sulfone and sulfoxide monomers 5 and 6.

Polysulfone 1 was synthesized by polycondensation of BHDB and bis(4-fluorophenyl)sulfone in sulfolane to afford polymer products with relatively high molecular weight (M<sub>n</sub> approaching 50 kDa) relative to PMMA standards. These solution polymerizations were conducted at 170-180 °C for 2-3 h using magnetic stirring under a  $N_{2(g)}$  atmosphere. While other polar aprotic solvents, such as dimethylsulfoxide (DMSO) or N-methylpyrrolidone (NMP) could be used, sulfolane was preferred for the high reaction temperatures it allows, and toluene (10 mL) was added to the reaction mixture to afford an anhydrous system by its azeotropic distillation with water. The polymerization mixture was heated to 140-150 °C while stirring for 2 h, then to 180 °C under constant purging with N<sub>2(g)</sub>. The mixture was cooled to room temperature, diluted with dichloromethane, and precipitated into methanol/ acetic acid. The precipitated polymer was collected by filtration, redissolved in dichloromethane, and filtered through Celite to remove inorganic salts. The polymer was purified further by precipitation into methanol, then isolated by filtration as a white fibrous material. <sup>1</sup>H NMR spectroscopy of polysulfone **1** in CDCl<sub>3</sub> showed a signal for the methylene protons of BHDB at 4.30 ppm, while <sup>13</sup>C NMR revealed the carbonyl carbon resonance of the deoxybenzoin moiety at 196 ppm, a signal at 44.5 ppm for the methylene carbon, and aromatic resonances from 115 to 162 ppm. Aromatic polysulfoxides 2 were synthesized similarly, using bis(4fluorophenyl)sulfoxide as the sulfoxide monomer, which was synthesized by Friedel-Crafts acylation of fluorobenzene with thionyl chloride.[42].

The polymerization of BHDB with bis(4-fluorophenyl)sulfone was conducted over 2 h to afford polysulfone **1** of molecular weight Mn 18,400 and Mw 57,000 (Mn = number-average molecular weight; Mw = weight-average molecular weight). Under similar conditions, BHDB polymerization with sulfoxide **6** affording polysulfoxide **2** proceeded more slowly, requiring 15 h to afford polymer samples of Mn 13,400 and Mw 43,500. The faster polymerization in the sulfone case is attributed to its greater electron withdrawing capacity and C–F bond activation. [41,42] The temporal evolution of molecular weight was monitored by gel permeation chromatography (GPC) against PMMA calibration standards, performed on aliquots taken at several time intervals during the course of the polymerization (shown in Fig. 2 for polysulfoxide **2**).

Copolymerization of BHDB with bis(4-fluorophenyl)sulfone and 4,4'-biphenol or 4,4'-thiodiphenol (Scheme 2) was performed in sulfolane in the presence of potassium carbonate to afford the desired polymers **9** and **10**. The polymer products were soluble in common organic solvents, and casting from ~2 to 5 mg/mL dichloromethane solution produced transparent flexible films, such as seen for polysulfone **10** in Fig. 3.

These films exhibited excellent properties, judged qualitatively, with apparent transparency and amenability to manual folding and



Fig. 2. Plot of number-average molecular weight as a function of time (hrs) for polysulfoxide 2.

creasing without inducing damage. The relative ratio of the two bisphenols (4,4'-thiodiphenol and BHDB) incorporated into polysulfone **10** was calculated by integration of the solution <sup>1</sup>H NMR spectra. For example, the singlet at  $\delta$  4.33 ppm representing the two methylene protons of the deoxybenzoin was integrated against the resonance at  $\delta$  7.36 ppm for the four aromatic protons adjacent to the sulfur of 4,4'-thiodiphenol. <sup>13</sup>C NMR spectroscopy showed signals at 197.3 and 45.5 ppm, representing the deoxybenzoin carbonyl and methylene groups, respectively. Infrared spectroscopy confirmed the expected carbonyl content in the copolymer, with characteristic stretching at 1678 cm<sup>-1</sup>, and additional bands at 1163 cm<sup>-1</sup> and 1103 cm<sup>-1</sup> reflecting the sulfone functionality. Molecular weights and polydispersity indices (PDI, Mw/Mn) of these polymers were measured by GPC in DMF against PMMA standards (Table 1). In the samples used for GPC in Fig. 4 (plotting retention time vs. refractive index intensity), polymer 10 had an estimated Mn of 48,100 g/mole, and polymer 9 34,000 g/mole, with respective PDI values of 2.6 and 1.9 that are typical outcomes of step growth polymerization.

Thermal characterization and heat release measurements. All of the synthesized polymers exhibited a glass transition temperature (Tg) indicative of an amorphous or glassy morphology. The presence of deoxybenzoin reduced the Tg relative to a commercially available poly(aryl ether) (220 °C) [43]: for example copolymers 9 and 10 had Tg values of 200 and 172 °C respectively, whereas polymers 1 and 2 showed Tg values of 173 and 150 °C (Table 1). These deoxybenzoin-containing polymers exhibit significant thermal stability, with decomposition temperatures in the 375-470 °C range at 5% weight loss. The presence of deoxybenzoin in the polymer backbone impacts decomposition onset, T<sub>d</sub>, as shown in Fig. 5. Char yields at 800 °C, revealed by TGA measurements, for deoxybenzoin-containing polysulfone **1** and polysulfoxide **2** were 42% and 54%, respectively, whereas char yields of the polysulfone copolymer 9 and polysulfone-sulfide copolymer 10 were 46% and 43% respectively.

Thermal characterization of these sulfur-containing deoxybenzoin polymers revealed exceptionally low heat release capacity (HRC) values of <70 J g<sup>-1</sup> K<sup>-1</sup>, and a total heat release (THR) of <7 kJ/g. This data, obtained by pyrolysis combustion flow calorimerty (PCFC), an oxygen consumption technique, places these novel deoxybenzoin containing polymers in the ultra-low flammability category, despite the absence of halogen in the structure.

Similarly constructive data was obtained in PCFC analysis: polymer **2**, having a char yield of 54%, exhibited HRC of 66 J/g-K and THR of 6.5 kJ/g, a significant reduction relative to the commercially available homopolymer (polymer **9** (m = 0) has a reported HRC of 228 J/g-K and THR of 13.5 K J/g (Table 2). [44] Pyrolysis combustion flow calorimetry (PCFC) revealed that the HRC and THR values of the new polymers prepared decreased significantly with increasing incorporation of deoxybenzoin moieties (defining HRC as the



Scheme 2. Copolymerization of BHDB with aromatic monomers 5,7 and 8.



Fig. 3. Solution cast film of deoxybenzoin-containing polysulfone 10.

# Table 1

Data obtained for deoxybenzoin-containing polymers and copolymers with 4,4'biphenol and 4,4'-thiodiphenol.

Polymer	m	n	х	$T_g^a$ (°C)	T <sub>d</sub> <sup>b</sup> (°C)	<b>M</b> n <sup>c</sup> (g/mole)	Mw <sup>c</sup> (g/mole)	PDI <sup>c</sup>
1	0	1	SO <sub>2</sub>	173	452	18400	57000	3.1
2	0	1	SO	150	375	13400	43500	3.2
9	0.5	0.5	$SO_2$	200	439	34000	64000	1.9
10	0.5	0.5	SO <sub>2</sub>	172	468	48100	128000	2.6

<sup>a</sup> Obtained by DSC in N<sub>2</sub> at a heating rate of 10 °C/min.

<sup>b</sup> Measured by TGA in N<sub>2</sub> at a heating rate of 20 °C/min;  $T_d = 5\%$  weight loss temperature in N<sub>2</sub>.

 $^{\rm c}$  Determined by GPC in DMF at 1.0 mL/min at 50  $^{\circ}{\rm C}$  calibrated with PMMA standards.

maximum heat released divided by the heating rate). Describing these systems in terms of HRC eliminates reliance on heating rate that is typical of standard flammability measurements, rendering HRC a characteristic material property.[27–28]. THR is the total heat of complete combustion of the pyrolysis products per initial mass of the sample. Low HRC and THR values are thus useful indicators of flame retardancy, and predict non-flammable behavior in larger scale tests.[29] Microscale combustion calorimetry (MCC) characterization of the aromatic deoxybenzoin polysulfones **1** and polysulfoxides **2** revealed HRC values of 120 Jg<sup>-1</sup> K<sup>-1</sup> and 66 Jg<sup>-1</sup> K<sup>-1</sup>, and THR values of 10 kJ/g and 6.5 kJ/g, respectively,



**Fig. 4.** Overlaid GPC traces of polymers **1**, **2**, **9**, and **10** (y-axis is the refractive index (RI) response).



Fig. 5. TGA analysis (weight loss versus temperature) of polymers 1, 2, 9, and 10 under  $N_{\rm 2(g)}$  atmosphere.

while polysulfone copolymer **9** containing deoxybenzoin as a comonomer with equal molar amounts of 4,4'-biphenyl exhibited HRC of 86 Jg<sup>-1</sup> K<sup>-1</sup> and THR of kJ/g. (Fig. 6) Thus, introduction of deoxybenzoin into a polyphenylsulfone backbone leads to a substantial HRC reduction (Table 2) relative to a commercial polyphenylsulfone, [44] and opens opportunities for the use of these polymers in materials applications that benefit from low flamma-bility plastics.

In summary, we described the integration of deoxybenzoinbased monomers into sulfur-containing polymers, affording novel poly(aryl ether deoxybenzoin) sulfone, sulfoxide and sulfide

#### Table 2

Heat release capacity (HRC), total heat release (THR), and charring properties of deoxybenzoin-containing polymers and commercial polyether sulfone.

Entry	Polymer	m	n	Х	HRC [J g <sup>-1</sup> K <sup>-1</sup> ]	THR [KJ g <sup>-1</sup> ]	Char <b>[%]</b> <sup>a</sup>
1	BHDB-sulfone (1)	0	1	SO <sub>2</sub>	120	10	42
2	BHDB-sulfoxide (2)	0	1	SO	66	6.5	54
3	BHDB/biphenyl (9)	0.5	0.5	$SO_2$	86	8	46
4	BHDB/sufide (10)	0.5	0.5	$SO_2$	138.5	10.7	43
5	Poly (aryl ether) ( <b>9</b> ) <sup>b</sup>	0	1	$SO_2$	228 <sup>b</sup>	13.5 <sup>b</sup>	С

<sup>a</sup> Obtained from TGA at 800 °C in nitrogen (heating rate 20 °C min<sup>-1</sup>).

<sup>b</sup> Data obtained from reference [44].

<sup>c</sup> Not determined.



Fig. 6. Heat release rate (HRR) verses temperature for polymers 1, 2, 9 and 10.

polymers having low heat release properties and amenability to solution processing. Integration of deoxybenzoin units as comonomers considerably reduces the heat release capacity values of commercial aromatic polysulfones and other engineering thermoplastics, and further studies detailing the use of these new polymers in blends, and their resultant mechanical properties, will be reported subsequently.

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