



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



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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 fire-related 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

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 phosphonate-containing 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-(1-pyridino)-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 nanoclay particles and the formation of a continuous protective solid carbonaceous layer 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 ethynyls 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<sub>2(g)</sub> 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<sub>2(g)</sub> 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 cm<sup>3</sup>/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 × 7.5 mm PL gel mixed guard column, one 300 × 7.5 mm PL gel 5 μm mixed C column, one 300 × 7.5 mm PL gel 5 μm 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): δ 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-CH<sub>2</sub>-Ar). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>): δ 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

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