Macromolecules **2006,** *39,* 3553−3558

Deoxybenzoin-Based Polyarylates as Halogen-Free Fire-Resistant Polymers

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Received December 30, 2005; Revised Manuscript Received March 15, 2006

ABSTRACT: The synthesis, processing, and engineering of halogen-free, low heat release, fire-resistant materials present important challenges in polymer materials chemistry. One approach to this problem involves the use of polymers that char upon decomposition, reducing the evolution of flammable gas and acting as an insulating layer. Demonstrated here is the synthesis of novel char-forming polyarylates prepared by interfacial polycondensation of 4,4′-bishydroxydeoxybenzoin (BHDB) and isophthaloyl chloride. A variety of copolyarylates containing BHDB, bisphenol A (BPA), and isophthaloyl chloride were prepared and shown to exhibit superior fire resistance to many polymers in the low flammability category. A char yield of 42% and heat release capacity of 62 J/(g K) were measured for the BHDB-containing polyarylate, while polyarylates containing both BHDB and BPA combined desirable fire-resistant properties with appreciable polymer solubility and processability.

Introduction

The extensive application of polymer materials in society requires research efforts directed toward improving their fire resistance. Small molecule flame-retardant additives provide a convenient means for reducing flammability of some materials, but these additives may compromise material properties due to additive leaching and also may pose environmental problems associated with toxicity, bioaccumulation, and recycling.[1,2] Halogenated flame retardants such as polybrominated biphenyl (PBBs) have been banned in Europe, Japan, and the United States.[1] Brominated diphenyl ether flame retardants have likewise been identified as environmental hazards[3,4] and may face legislative restrictions.[1,5,6] Nonhalogenated flame retardants may also present problems, such as some examples of phosphorus-containing polymers with high carbon monoxide emission.[7,8] Ideal flame-retardant polymers would possess high thermal stability, low combustion heat release rate, low total heat of combustion, and minimal release of toxic fumes. The use of nonhalogenated polymers that undergo significant carbonization upon heating is highly desirable, as char formation effectively precludes the combustion process.

Polymers derived from the bisphenol of chloral, or 1,1-dichloro-2,2-(4-hydroxyphenyl)ethane (BPC), show exceptionally good fire resistance.[9−20] Investigations into decomposition pathways of BPC-containing polymers suggest that char formation may proceed through diphenylacetylene derivatives, arising either from base-induced elimination of chlorine on BPC to give a carbene, which undergoes phenyl migration to diphenylacetylene (Scheme 1), or through multiple proposed steps at elevated temperatures.[21−23] Thus, while chlorine in BPC sets up the rearrangement chemistry, the role of diphenylacetylene must be of considerable importance. Efforts toward nonhalogenated precursors with such char-forming properties provide the impetus for this work.

Walters and Lyon reported pyrolysis combustion flow calorimetry (PCFC), an oxygen consumption calorimetry method that measures the heat release capacity and total heat release of polymer materials.[24−27] Heat release capacity is the peak heat release rate normalized to the heating rate, determined by oxygen consumption methods.[24] An attractive feature of PCFC for obtaining heat release capacity values is its capability to analyze milligram scale samples. Table 1 gives thermal properties of a variety of commercial polymers, including heat release capacity, total heat release, and char yield. The development of polymers with heat release properties equal to or better than polymers such as poly(ether ether ketone) and poly(etherimide) is especially important. From Table 1 it can be seen that BPC−polycarbonate and polyarylate possess lower heat release capacity and total heat release values; nonhalogenated versions with such properties would be ideally suited for introduction into large-scale commercial applications.

Zwanenburg and co-workers reported the catalyzed conversion of deoxybenzoin to diphenylacetylene by flash vacuum pyrolysis at 300−500 °C.[28] The temperature range at which deoxybenzoin goes to diphenylacetylene suggests its potential utility to effect char in burning polymer materials. To our knowledge, the bisphenol of deoxybenzoin has not been used previously as a monomer in polymer synthesis. However, this bisphenol monomer has considerable promise in condensation polymers, given the rich polymerization chemistry of bisphenols, such as BPA, and the range of polymer materials into which it could be incorporated. Thus, the synthesis of novel polyarylates derived from the bisphenol of deoxybenzoin is reported here, as well as an investigation of the thermal properties of these novel polymers.

Results and Discussion

4,4′-Bishydroxydeoxybenzoin (BHDB) was prepared by demethylation of desoxyanisoin in molten pyridine hydrochloride, according to a literature procedure.[29] Recrystallization from acetic acid gave BHDB in 80−85% yield on the 100 g scale. Scheme 2 depicts the interfacial polycondensation of BHDB with isophthaloyl or terephthaloyl chloride to give

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Scheme 1

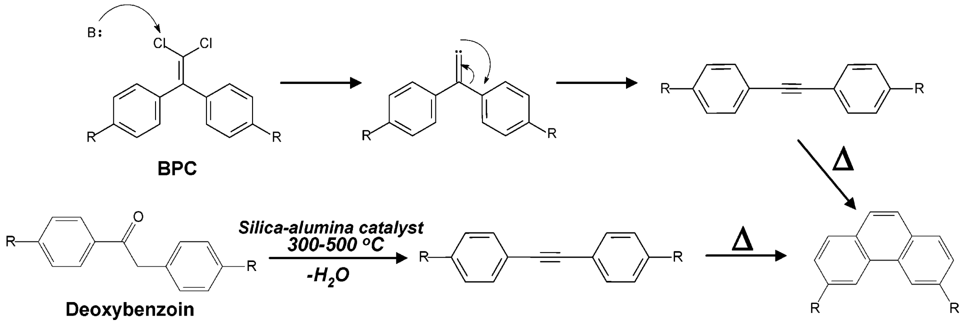


Table 1. Heat Release Capacity, Total Heat Release, and Char Yield for Some Commerical Polymers (BPA−Bipshenol A; BPC−Bisphenol of Chloral)[24]

polymer	heat release capacity (J/(g K))	total heat release (kJ/g)	char yield (%)
polyethylene	1676	41.6	0
polystyrene	927	38.8	0
BPA polycarbonate	359	16.3	21.7
poly(ethylene terephthalate)	332	15.3	5.1
poly(ether ether ketone)	155	12.4	44.5
poly(etherimide)	121	11.8	49.2
BPC polycarbonate	29	3.0	50.1
BPC polyarylate	21	7.6	42.7

deoxybenzoin-containing polyarylates **1** and **2**. The disodium salt of BHDB was prepared by stirring BHDB in aqueous NaOH; then, the phase-transfer catalyst benzyltriethylammonium chloride was added, followed by a dichloromethane solution of one or both of the diacid chlorides. The BHDB-containing polyarylates **1** and **2** were seen to precipitate during the course of polymerization. Polyarylate **2**, containing BHDB and terephthaloyl chloride, was insoluble in all solvents tested. However, polyarylate **1**, containing BHDB and isophthaloyl chloride, dissolved in DMSO and DMF at elevated temperatures (above 60 °C).

As polyarylates derived from BPA are soluble in common organic solvents,[30,31] soluble versions of BHDB-containing polyarylates were obtained by copolymerization of BPA, BHDB, and isophthaloyl chloride, as shown in Scheme 3. As shown in Table 2, a range of feed ratios of the two bisphenol comonomers was employed in the preparation of copolyarylates **3**−**14**; polymerization yields, solubility, and molecular weight estimation for these polymers are also given in Table 2. In general, the solubility of BHDB-containing polyarylates was found to increase with BPA content. BPA:BHDB ratios of 3:2 or greater gave polymers with solubility in chloroform; copolymers with higher levels of BHDB in the structure had lower solubility in general but could still be dissolved in DMF. Following initial precipitation, Soxhlet extraction with methanol was used to purify the polymer products by removal of any unreacted BHDB and low molecular weight oligomers. Removal of these low molecular weight materials accounts for the unusually narrow polydispersity values, and modest yields, for the condensation polymers reported in Table 2.

The relative ratio of the two bisphenols (BPA and BHDB) incorporated into the polyarylate backbone was calculated for copolymers **3**−**13** by integration of the ^{1}H NMR spectra. For example, in polymer **5**, the singlet at δ 1.73 ppm for the BPA methyl groups can be integrated against the resonance at δ 4.52 ppm for the methylene groups of deoxybenzoin monomer units. Moreover, the aromatic signals of the isophthaloyl groups (δ 8.9, δ 8.5, and δ 7.7 ppm) are baseline-separated from the aromatic signals (δ 7.1−7.6 ppm) for the BPA and BHDB components of the polymer. ^{13}C NMR spectroscopy provided further evidence for the success of this copolymerization. In polymer **5**, for example, the carbonyl resonance from the deoxybenzoin units was found at δ 196.2 ppm, and signals at δ 31.2 and 45.0 ppm were noted for the methyl groups and quaternary carbon, respectively, of BPA. A signal at δ 42.8 ppm is assigned to the α-ketone methylene group, and the remaining signals in the aromatic region are consistent with those expected from BPA, BHDB, and isophthaloyl units.

In general, BPA was found to be incorporated into polyarylates more readily than BHDB. This is reflected in Table 2 by examination of the incorporated vs feed ratios of the two bisphenol comonomers. This observation is likely due to the more equal reactivity of the BPA phenols relative to those of BHDB due to the electronic influence of the carbonyl group of BHDB on one of the phenols. As a control experiment, standard Schotten−Baumann acylation conditions[32] were performed on BHDB with benzoyl chloride (1 equiv per phenol) at 0 °C, using sodium hydroxide as base. While the major product was found to be the disubstituted product, about 20% of the product was monosubstituted at the phenol on the “methylene side” of the molecule. In contrast, BPA under identical conditions forms the disubstituted product exclusively. This unequal reactivity of the phenolates in BHDB must be a limiting factor in the polycondensation, keeping the molecular weights modest. Optimization of reaction conditions toward higher molecular weights in BHDB-containing polymers is ongoing.

Thermal Properties of BHDB-Containing Polyarylates. The thermal conversion of deoxybenzoin to diphenylacetylene derivatives in these polyarylates is expected to lead to char formation, which should increase with deoxybenzoin monomer content. Table 3 summarizes heat release (HR) capacity and total heat release obtained for polymers **1**−**14** from PCFC. As seen in Table 3, heat release capacity decreases with increasing mole percent BHDB. For example, the heat release capacity of polymer **1** was found to be 61.5 J/(g K), substantially lower than 456.3 J/(g K) (for BPA−polyaryate **14**). The polyarylates containing as high as 30 mol % BPA segments gave heat release capacities under 100 J/(g K), well below that of poly(etherimide) (121 J/(g K)). Moreover, it is evident from Table 3 that increasing amounts of deoxybenzoin in these copolyarylates results in increased char yield (from 26% to 42% at 800 °C). The temperatures at which 5% weight loss occurs for the BHDB polyarylate and other copolyarylates were in the range 330−350 °C, whereas the corresponding temperature for BPA−polyarylate was 425 °C.

To study the potential of BHDB as an alternative to BPC in flame-retardant polymers, copolyarylates containing both BPC and BPA in the backbone were prepared,[12,14] and their thermal properties were compared to those of the BHDB/BPA copolymers. BPC/BPA copolymers **15**−**20** were prepared using

Scheme 2

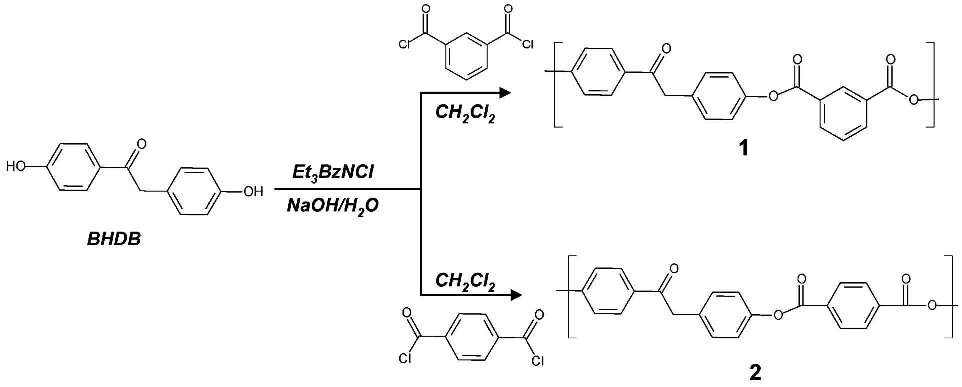


Table 2. Compositions, Solubility, Yields, and Molecular Weight Data for Polyarylates 1−14

polymer	BHDB:BPA feed	BHDB:BPA incorporated[a]	yield (%)	GPC[b] M_w	GPC[b] M_n	GPC[b] PDI	GPC[b] solvent
1	100:0	100:0	64	3200	2600	1.22	DMF
2[c]	100:0	100:0	47				insoluble[d]
3	90:10	87:13	42	7200	5900	1.22	DMF
4	80:20	78:22	43	4400	3200	1.37	DMF
5	70:30	70:30	60	4200	3400	1.24	DMF
6	60:40	53:47	49	4700	3300	1.42	DMF
7	50:50	41:59	72	4100	3300	1.20	$CHCl_3$
8	40:60	27:73	54	19000	13400	1.39	$CHCl_3$
9	40:60	23:77	42	15100	8900	1.65	$CHCl_3$
10	35:65	21:79	40	8700	5100	1.26	$CHCl_3$
11	30:70	14:86	42	7800	6300	1.23	$CHCl_3$
12	20:80	12:88	56	5800	3900	1.49	$CHCl_3$
13	10:90	7:93	85	11400	5100	2.25	$CHCl_3$
14	0:100	0:100	66	20300	11200	1.81	$CHCl_3$

[a] Ratio of the two bisphenol comonomers as calculated by proton NMR integration. [b] GPC analysis against polystyrene standards. [c] Terephthaloyl chloride as diacid chloride. [d] Insoluble in common organic solvents such as DMSO, DMF, chloroform, and THF.

Scheme 3

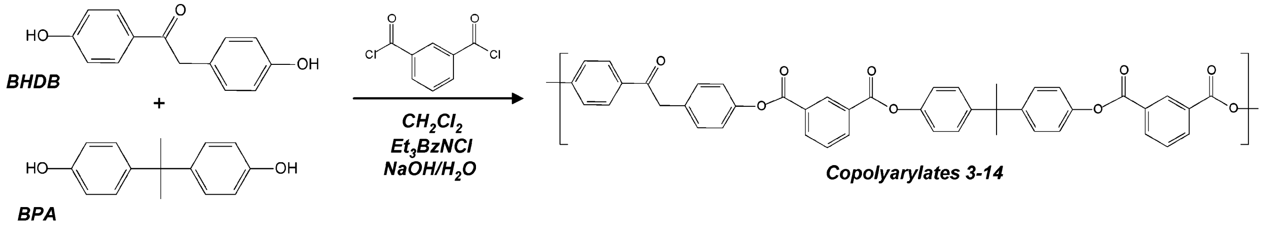


Table 3. PCFC and TGA Data for the Polyarylates 1−14

polymer	composition (BHDB:BPA)	heat release capacity (J/(g K))	total heat release (kJ/g)	char yield (%) PCFC	char yield (%) TGA
1	100:0	61.5	7.5	43.7	42.2
3	87:13	63.7	7.5	46.6	42
4	78:22	73.9	8.9	45.0	40.4
5	70:30	80.9	10.8	40.4	37.4
6	53:47	148.5	12.3	33.6	36.9
7	41:59	158.8	12.8	32.1	33.7
8	27:73	165.3	12.9	37.8	32.8
9	23:77	166.4	13.2	35.3	32.5
10	21:79	168.8	13.0	37.3	32.9
11	14:86	236.7	13.1	38.3	30.5
12	12:88	272.3	15.9	25.7	26.4
13	7:93	317.1	16.2	26.3	28.9
14	0:100	456.3	17.7	25.5	25.8

isophthaloyl chloride as the diacid chloride (Scheme 4), such that meaningful comparisons could be made across the range of polymers prepared. These polyarylates were obtained in 80−90% yields in 1−2 h. In some cases, a minor amount of insoluble material was obtained, and in all cases the chloroform-soluble portion of the isolated copolymer was used for characterization and analysis. Molecular weight estimation by GPC of polyarylates **15**−**20** in chloroform revealed high molecular weights (against linear polystyrene calibration standards with higher BPA feed ratios), as given in Table 4.

Thermal degradation data for BPC/BPA copolyarylates given by PCFC and TGA analysis is given in Table 4. Increasing mole percent of BPC monomer units into these copolyarylates gave, as expected, better flame-resistant behavior, as seen from the rapid decrease in heat release capacity. TGA studies of these copolyarylates revealed high char yields (∼30−50%) upon increasing mole percentage of BPC units. These copolymers also showed excellent thermal stability; 5% weight loss was typically seen in the temperature range 410−430 °C.

Figure 1 overlays plots of the heat release capacity of BPC/BPA, and BHDB/BPA copolyarylates, against mole percentages of the respective flame-resistant monomers BPC and BHDB. Both sets of copolymers showed similar trends, in that polymer flammability decreased with increasing BHDB or BPC content. Ultimately, the BPC-containing polymers show better flame-resistant properties. However, it is particularly striking that integration of relatively low mole percentages (10−20%) of BHDB comonomer results in very substantial decreases in heat release capacity. Moreover, it is in this BHDB:BPA monomer

Scheme 4

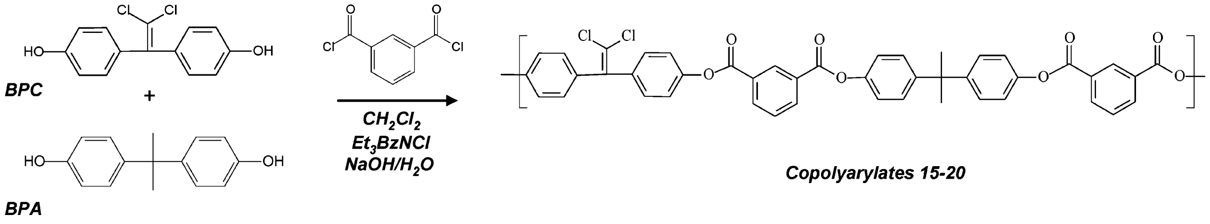


Table 4. Thermal Properties of Copolymers Based on BPC and BPA

polymer	composition (BPC:BPA) feed	composition (BPC:BPA) incorporated[a]	yield (%)[b]	GPC[c] M_w (PDI)	heat release capacity (J/(g K))	total heat release (kJ/g)	char yield (%)[d] PCFC	char yield (%)[d] TGA
15	100:0	100:0	55	7500 (2.25)	12.9	3.73	49.8	52
16	70:30	68:32	75	8600 (2.26)	22.3	5.2	58	56.5
17	60:40	57:43	65	76500 (1.66)	34	8.3	48.6	46.7
18	50:50	42:58	65	98100 (3.06)	66.3	4.8	52.1	51.7
19	40:60	39:61	74	73500 (2.48)	83	7.4	48.9	52.2
20	30:70	26:74	82	134300 (2.52)	199	10.6	36.8	48.5
14a	0:100	0:100	53	137500 (2.06)	344	14.2	27.4	31.2

[a] Ratio of the two bisphenol comonomers as calculated by proton NMR integration. [b] Yields for the chloroform soluble fractions of the polymers. [c] GPC analysis against polystyrene standards in chloroform solvent. [d] Char yield at 900 °C.

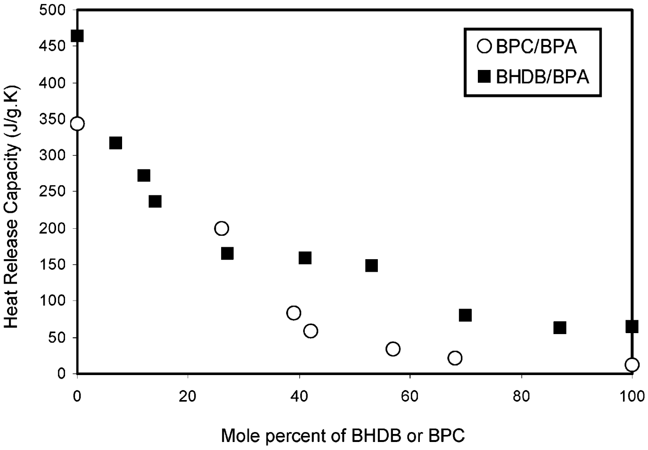


Figure 1. Overlaid plots of heat release capacity vs mole percent BPC and BHDB as comonomers with BPA.

ratio range that the BHDB–BPA copolyarylates exhibit good solubility and processability. Thus, these polymers may be considered excellent candidates for further exploration toward flame-resistant, halogen-free polymer materials.

Synthetic Variants of BHDB-Containing Copolymers. The limited solubility of polyarylates **1** and **2**, combined with the opportunities for α-ketone-substituted BHDB derivatives, led to the preparation of an alkylated derivative **22** and its use as a monomer in polycondensation chemistry. 1,2-Bis(4-hydroxyphenyl)decan-1-one (**22**) was synthesized as shown in Scheme 5, by deprotonation of desoxyanisoin with NaH in THF, followed by alkylation with 1-bromooctane to afford 1,2-bis(4-methoxyphenyl)decan-1-one (**21**). Bisphenol **22** was then prepared by treatment of **21** with pyridine hydrochloride, similar to that described previously for BHDB. The interfacial polycondensation of **22** with isophthaloyl chloride, also using conditions similar to those described above, gave polyarylate **23**. Polymer **23** was found to be readily soluble in chloroform, with GPC-estimated molecular weight M_w of 21 800 and a polydispersity index of 3.81. TGA experiments on polyarylate **23** gave a char yield of 27% at 800 °C, and PCFC evaluation gave a heat release capacity of 285 J/(g K) and total heat release of 18.9 kJ/g. The higher level of flammability of polymer **23** relative to the unalkylated BHDB family of polymers was expected from the fuel provided by the *n*-octyl chains. Nonetheless, the successful preparation of substituted BHDB-type polymers is encouraging, and other derivatives are envisioned that contain α-ketone functionality designed to enhance properties including but not limited to flame resistance, solubility, miscibility with other polymers in blends, and surface-active functionality.

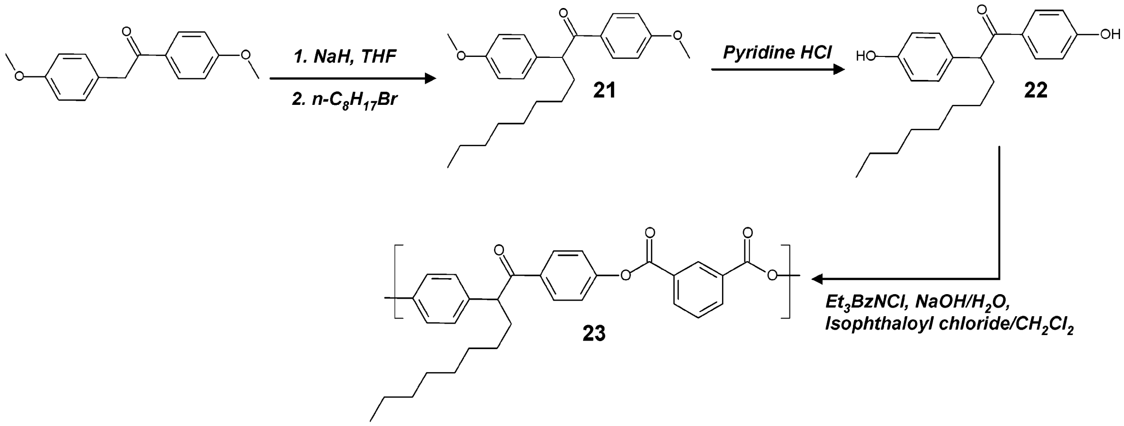
In summary, a new type of halogen-free, fire-resistant polyarylate was prepared by interfacial polycondensation of isophthaloyl chloride with different relative ratios of the bisphenols 4,4′-bishydroxydeoxybenzoin (BHDB) and bisphenol A (BPA). The flame-resistant properties of these polyarylates were investigated by TGA and PCFC, and the potential utility of BHDB as a replacement for halogenated low heat release materials such as BPC was demonstrated. While the present studies already indicate the special nature of this previously unused bisphenolic monomer in flame-resistant polymers, the future of such materials is open for exploration, especially for (1) variation of α-ketone substituents and (2) use of BHDB as precursors to other classes of polymer materials such as epoxies. Both of these topics are under investigation in our laboratories at this time. Moreover, the well-known solution photolability, and solid-state photostability,[33] of the benzoin moieties offers an additional parameter that can be utilized in new materials design and application.

Experimental Section

Materials. Bisphenol A, desoxyanisoin, pyridine hydrochloride, isophthaloyl chloride, terephthaloyl chloride, benzyltriethylammonium chloride, 1-bromooctane, and sodium hydride were purchased from Sigma-Aldrich and used as received, unless otherwise stated. Dichloromethane was washed with sulfuric acid and distilled over calcium hydride. Tetrahydrofuran was distilled over sodium and benzophenone.

Instruments. NMR spectra were recorded on either $CDCl_3$ or DMSO-d_6 solutions using a Bruker DPX300 or Bruker Avance400 spectrometer referenced to residual $CHCl_3$ or DMSO. Infrared spectra were obtained on a Perkin-Elmer Spectrum One FT-IR spectrometer equipped with an ATR accessory. HRMS-FAB data were acquired on a JEOL JMS 700 mass spectrometer. Molecular weights and polydispersity indices were measured by gel permeation chromatography in chloroform or DMF relative to polystyrene standards on systems equipped with three-column sets (Polymer Laboratories 300 mm × 7.5 mm, 5 μm, 10^{-5}, 10^{-4}, and 10^{-3} Å pore sizes) and refractive index detectors (HP 1047A) at 35 °C

Scheme 5



(chloroform) or 50 °C (DMF) with a flow rate of 1 mL/min. Thermogravimetric analysis was performed in a nitrogen atmosphere on a DuPont TGA 2950 using a ramp rate of 10 °C. Heat release capacity and total heat release were measured using pyrolysis combustion flow calorimetry (PCFC),[24−28] where the average of five samples of 1−5 mg (±0.1 mg) were pyrolyzed in nitrogen from 100 to 900 °C at a heating rate of 1 °C/s, and the evolved gases were combusted with excess oxygen at 900 °C.

4,4′-Bishydroxydeoxybenzoin (BHDB). This compound was prepared as described previously,[29] though characterization data are presented here for the first time. Desoxyanisoin (50 g, 195.1 mmol) and pyridine hydrochloride (90.2 g, 780.5 mmol) were added to a round-bottom flask equipped with a condenser and magnetic stirbar. The mixture was refluxed (200 °C) for 5 h, cooled to room temperature, poured into water, filtered, and crystallized from acetic acid to afford the desired product as a white crystalline solid (38 g, 85%). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 10.35 (s, 1H, O*H*−Ar−CO), 9.28 (s, 1H, O*H*−Ar−CH$_2$), 7.91 (d, 2H, J = 8.7 Hz, Ar−*H*), 7.04 (d, 2H, J = 8.5 Hz, Ar−*H*), 6.84 (d, 2H, J = 8.7 Hz, Ar−*H*), 6.68 (d, 2H, J = 8.5 Hz, Ar−*H*), 4.11 ppm (s, 2H, Ar−CO−C*H*$_2$−Ar). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 196.5, 162.3, 156.2, 131.3, 130.7, 128.1, 125.9, 115.5, 115.4, 43.7 ppm. FT-IR ν 3340 (C−OH, vs), 3024 (C−H aromatic, w), 2895 (C−H aliphatic, w), 1664 (O═C, s), 1591 (C═C aromatic, s), 1513 (C═C aromatic, m), 1443 (C═C aromatic, m), 1344, 1277, 1203, 1209, 1166, 826. HRMS−FAB *m/z* [M + H]$^+$ calcd 229.0865; found 229.0868.

Polyarylate 5. A solution of sodium hydroxide (2.17 g, 54.25 mmol) in water (35 mL) was added to a 250 mL round-bottom flask containing a magnetic stir bar, bisphenol A (0.882 g, 3.869 mmol), 4,4′-bishydroxydeoxybenzoin (2.06 g, 9.035 mmol), and benzyltriethylammonium chloride (147 mg, 0.645 mmol). To this was added dropwise by addition funnel a solution of isophthaloyl chloride (2.62 g, 12.89 mmol) in dichloromethane (65 mL), and the two-phase system was stirred vigorously for 2 h. The mixture was then poured into methanol (500 mL), filtered and washed with water (3 × 50 mL), and then with methanol (3 × 50 mL) to afford a white fibrous solid (2.7 g, 60%). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 8.79 (s, 1H, isophthaloyl aromatic), 8.49 (m, 2H, isophthaloyl aromatic), 8.14 (d, 2H, J = 8.5 Hz, Ar−*H*), 7.7 (m, 1H, isophthaloyl aromatic), 7.69 (m, 2H, Ar−*H*), 7.38 (d, 2H, J = 8.5 Hz, Ar−*H*), 7.34 (d, 2H, J = 8.5 Hz, Ar−*H*) 7.32 (d, 2H, J = 8.6 Hz, Ar−*H*), 7.24 (d, 2H, J = 8.5 Hz, Ar−*H*), 7.17 (d, 4H, J = 8.6 Hz, Ar−*H*), 4.52 (s, 2H, Ar−CO−C*H*$_2$−Ar), 1.72 (s, 6H, Ar−C(C*H*$_3$)$_2$−Ar) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ 196.2, 164.5, 164.4, 163.9, 154.7, 150.0, 148.9, 148.8, 148.5, 148.4, 135.5, 135.2, 134.5, 132.5, 132.3, 132.0, 131.9, 130.9, 130.8, 130.7, 130.6, 130.5, 130.1, 129.9, 129.4, 129.3, 128.2, 122.2, 122.0, 121.9, 121.2, 117.4, 114.1, 45.0, 42.8, 31.2 ppm. FT-IR ν 3069 (C−H aromatic, w), 2969 (C−H aliphatic, w), 1734 (O═C, s), 1684 (O═C, m), 1599 (C═C aromatic, m), 1506 (C═C aromatic, m), 1299, 1194, 1162, 1062, 1016, 718 cm^{-1}.

1,2-Bis(4-methoxyphenyl)decan-1-one (21). To a solution of desoxyanisoin (2 g, 7.81 mmol) in tetrahydrofuran (20 mL) under a nitrogen atmosphere was added sodium hydride (0.28 g, 11.66 mmol). The mixture was stirred for 2 h at room temperature. A solution of 1-bromooctane (2.26 g, 11.71 mmol) in tetrahydrofuran (10 mL) was then added, and the suspension was refluxed for 8 h. The reaction mixture was brought to room temperature, poured into crushed ice, and extracted with ethyl acetate (3 × 30 mL). The organic layers were combined, washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The resulting yellow viscous solid was placed on silica gel and eluted with ethyl acetate/hexane mixture (10/90) to afford a white solid (2.7 g, 93%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.99 (d, 2H, J = 8.9, Ar−*H*), 7.26 (d, 2H, J = 8.7 Hz, Ar−*H*), 6.88 (d, 2H, J = 8.9 Hz, Ar−*H*), 6.84 (d, 2H, J = 8.7 Hz, Ar−*H*), 7.38 (d, 2H, J = 8.5 Hz, Ar−*H*), 4.48 (t, 1H, J = 7.3 Hz, CH$_2$−C*H*−Ar), 3.81 (s, 3H, Ar−O−C*H*$_3$), 3.75 (s, 3H, Ar−O−C*H*$_3$), 2.15 (m, 1H, Ar−CH−C*H*H−CH$_2$), 1.81 (m, 1H, Ar−CH−CH*H*−CH$_2$), 1.26 (m, 12H, CH$_2$−(C*H*$_2$)$_6$−CH$_3$), 0.892 ppm (t, 3H, J = 7.0, CH$_2$−C*H*$_3$). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 199.0, 163.3, 158.6, 132.5, 131.0, 130.1, 129.3, 114.3, 113.8, 55.5, 55.3, 52.5, 34.2, 32.0, 29.8, 29.6, 29.4, 27.9, 22.8, 14.2 ppm. FT-IR ν 2924 (C−H aromatic, s), 2854 (C−H aromatic, m), 1671 (C═O, s), 1599 (C═C aromatic, s), 1575 (C═C aromatic, w), 1509 (C═C aromatic, s), 1463 cm^{-1} (C═C aromatic, w). HRMS−FAB *m/z* M$^+$ calcd 369.2430; obsd 369.2391.

1,2-Bis(4-hydroxyphenyl)decan-1-one (22). 1,2-Bis(4-methoxyphenyl)decan-1-one (2.5 g, 6.87 mmol) and pyridine hydrochloride (3.18 g, 27.51 mmol) were added to a round-bottom flask equipped with a condenser and magnetic stirbar. The mixture was heated to 210 °C and allowed to reflux for 5 h. The reaction mixture was then cooled to room temperature, poured into 100 mL of cold water, and extracted with ethyl acetate (3 × 75 mL). The organic layers were combined, dried over magnesium sulfate, filtered, and concentrated under reduced pressure to give a dark yellow oil that was placed on silica gel and eluted with chloroform to give white crystalline solid (1.03 g, 45%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.86 (d, 2H, J = 8.7 Hz, Ar−H), 7.10 (d, 2H, J = 8.5 Hz, Ar−H), 6.82 (d, 2H, J = 8.7 Hz, Ar−H), 6.76 (d, 2H, J = 8.5 Hz, Ar−H), 4.45 (t, 1H, J = 7.2 Hz, CH$_2$−C*H*−Ar), 2.10 (m, 1H, Ar−CH−C*H*H−CH$_2$), 1.77 (m, 1H, Ar−CH−CH*H*−CH$_2$), 1.20 (m, 12H, CH$_2$−(C*H*$_2$)$_6$−CH$_3$), 0.84 ppm (t, 3H, J = 6.9 Hz, CH$_2$−C*H*$_3$). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 201.7, 161.2, 154.8, 131.9, 131.7, 129.5, 129.3, 116.1, 115.8, 52.5, 33.9, 32.0, 29.8, 29.6, 29.4, 27.8, 22.8, 14.3 ppm. FT-IR ν 3332 (C−OH, s), 2957, 2926, 2854, (C−H aliphatic, m), 1635 (O═C, m), 1593 (C═C aromatic, s), 1509 (C═C aromatic, m), 1440 (C═C aromatic, m), 1348, 1292, 1277, 1231, 1209, 1166, 834 cm^{-1}. HRMS−FAB *m/z* M$^+$ calcd 341.2117; obsd 341.2119.

Acknowledgment. The authors acknowledge financial support from the Center for UMass-Industry Research on Polymers (CUMIRP) and the supporters of flame-resistant polymer research within CUMIRP, including Boeing, the Federal Aviation Administration, the National Institute of Standards and Technology (NIST), Schneller, Inc., Solvay Advanced Polymers, and the U.S. Army. The authors also acknowledge the National Science Foundation Materials Research Science & Engineering Center (MRSEC) at UMass Amherst for facilities support. Dr. Richard Lyon is acknowledged for helpful discussions.

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MA052777O