

Synthesis and Characterization of Halogen-Free Antiflammable Polyphosphonates Containing 4,4'-Bishydroxydeoxybenzoin

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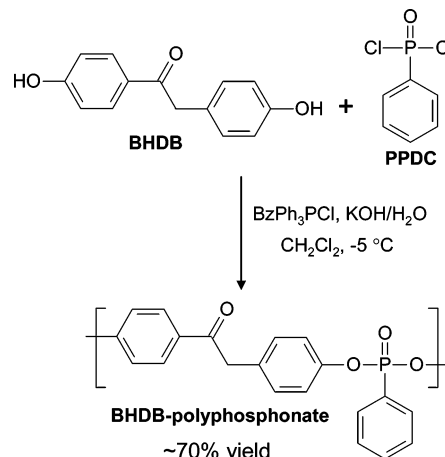
Received June 30, 2006

A significant drawback to many synthetic polymers is their inherent flammability. Polyethylene and polypropylene, for example, possess heat of combustion properties on par with low molecular weight hydrocarbons. Flame-retardant additives are often needed as a component of finished commercial polymer-based materials. Halogenated organic molecules, such as brominated aromatics, are particularly effective flame retardants but pose environmental and health hazards that are restricting their continued use.^{1–5} As such, there is a pressing need for new polymers with inherent flame resistance that do not contain halogen in the polymer structure and that do not require halogenated additives. Phosphorus-containing polymers are promising in this regard, as these polymers tend to char rather than burn.⁶ Charring provides a diffusion barrier of gaseous products to the flame, shields the polymer surface from heat and oxygen, and reduces the production of combustible gas during polymer degradation.⁷

We recently reported the synthesis of polyarylates that used 4,4'-bishydroxydeoxybenzoin (BHDB) as the bisphenolic monomer.⁸ These polymers exhibited low combustion heat release rate and total heat of combustion, which we believe arises from the thermally induced conversion of BHDB to diphenylacetylene moieties that char by aromatization.^{9,10} Pyrolysis combustion flow calorimetry (PCFC),¹¹ an oxygen consumption technique for measuring heat release capacity (HRC), revealed exceptionally low HRC values for the BHDB–polyarylates (<100 J/(g K)). However, the rather low solubility of these polyarylates limits their molecular weight and processability. When bisphenol A (BPA) and BHDB were used as co-bisphenols in the polyarylate synthesis, the solubility increased, but the flammability increased as well. Thus, as we report in this Communication, we chose to prepare BHDB-containing polyphosphonates, in an effort to combine ultralow flammability with good solubility and processability.

The novel polymers prepared in this study are the polycondensation products of phenylphosphonic dichloride (PPDC) and BHDB, as depicted in Scheme 1. Aromatic polyphosphonates based on PPDC exhibit excellent solubility and thermal stability.¹² Polymers prepared from PPDC and BPA possess HRCs of ~350–500 J/(g K), in the moderate flammability category and significantly above that of ultralow HRC (<100 J/(g K)) materials desired for use in transportation vehicles and enclosed spaces. Interfacial polymerization of BHDB and PPDC, using dichloromethane as the organic phase and benzyltriphenyl phosphonium chloride as the phase transfer catalyst, proved convenient for the synthesis of BHDB–polyphosphonate. Following polymerization, the polyphosphonate was purified by

Scheme 1. Synthesis of BHDB-Containing Polyphosphonates by Interfacial Polycondensation

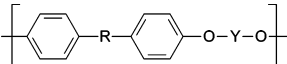


precipitation into hexane and isolated as a white solid. BHDB–PPDC polyphosphonates exhibit good-to-excellent solubility at room temperature in many solvents, including THF (70 mg/mL), chloroform (100 mg/mL), and DMF (400 mg/mL). Gel permeation chromatography (GPC) performed on DMF solutions (vs polystyrene standards) of these BHDB-containing polyphosphonates prepared by interfacial polymerization provided estimated molecular weights (M_w) of ~20 000 g/mol and polydispersity indices (M_w/M_n) of ~2.6.

³¹P NMR spectroscopy performed on DMSO-*d*₆ solutions of BHDB–polyphosphonate gave a signal centered at 12.7 ppm, in the expected region for an aromatic phosphonate. Expansion of this region showed the presence of three overlapping resonances, which correspond to head-to-head, head-to-tail, and tail-to-tail isomers that are a consequence of the unsymmetrical nature of BHDB. The infrared spectrum of BHDB–polyphosphonate showed the expected signals at 1440 (ν_{P-C}), 1270 ($\nu_{P=O}$), and 1204 cm^{-1} (ν_{P-O-C}) as well as a band at 1682 cm^{-1} arising from the carbonyl group. In the ¹H NMR spectrum, the BHDB methylene resonance was seen at 4.3 ppm, while ¹³C NMR spectroscopy showed the expected resonances for the aromatic carbons, the carbonyl carbon at 197.1 ppm, and the BHDB methylene carbon at 44.6 ppm.

PCFC analysis of the BHDB–polyphosphonate revealed exceptionally low HRC values of <100 J/(g K). These HRC values are superior to those of many known polymers already in the antiflammable category, such as poly(vinylidene fluoride) (311 J/(g K)), poly(phenylene sulfide) (165 J/(g K)), poly(ether ether ketone) (155 J/(g K)), poly(phenyl sulfone) (153 J/(g K)), poly(ether imide) (121 J/(g K)), and poly(ether sulfone) (115 J/(g K)).¹³ Polymers in the ultralow flammability category, such as bisphenol C polyether (16 J/(g K)), poly(ether ether ketone) (96 J/(g K)), and polybenzimidazole (36 J/(g K)), either are halogenated or possess the characteristically low solubility of rigid aromatic polymers. Table 1 compares HRCs of BHDB–polyphosphonate and BHDB–polyarylate against polyphosphonates and polyarylates containing the classic polycondensation monomer BPA. Replacing BPA with BHDB markedly lowers the HRC of the polymers, transforming them from moderately flame-resistant in the case of BPA to ultra-flame-resistant in the case of BHDB. Thermogravimetric analysis (TGA) of BHDB-containing polyphosphonates showed high thermal stability (5% weight loss observed at 345 °C) and char yields of

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Table 1. Measured Heat Release Capacities of BPA- and BHDB-Polyarylates⁸ and Polyphosphonates


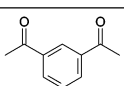
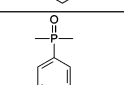
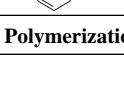
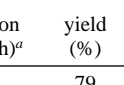
Bisphenol	R	Y	Heat release capacity, J/g·K	% Char (at 800 °C)
BPA	-C(CH ₃) ₂ -		344 ± 10	24
BHDB	-COCH ₂ -		62 ± 5	43
BPA	-C(CH ₃) ₂ -		365 ± 10	23
BHDB	-COCH ₂ -		81 ± 11	52

Table 2. Solution Polymerization of BHDB and PPDC

end-capping agent	reaction time (h) ^a	yield (%)	GPC ^b		
			M _w (g/mol)	M _n (g/mol)	PDI
2,6-Me ₂ PhOH	0.5	79	54 000	24 000	2.3
2,6-Me ₂ PhOH	1	75	116 000	40 000	2.9
2,6-Me ₂ PhOH	2	78	140 000	46 000	3.1
2,6-Me ₂ PhOH	4	86	55 000	23 000	2.4
phenol	2	75	138 000	46 000	3.0
phenol	3	79	165 000	44 000	3.8
phenol	5	80	52 000	22 000	2.6
phenol ^c	3	75	5 000	1 900	2.6
none	3	77	75 000	23 000	3.3

^a Reaction mixture stirred 1 h after adding end-capping agent. ^b DMF as eluent against polystyrene standards. ^c Without catalyst.

~50% at 800 °C. The high char yield of BHDB-containing polymers is a very attractive feature for deterring combustion of the polymer and lends support for a decomposition mechanism of BHDB proceeding through diphenylacetylene units that lead to char by aromatization.^{9,10}

Experiments were conducted to optimize the BHDB-PPDC polycondensation in an effort to obtain higher molecular weights than achieved by the interfacial method. The hydrolytic instability of PPDC may limit the effectiveness of the interfacial method, whereas solution polymerization of polyphosphonates can be conducted effectively under anhydrous conditions, as shown by McGrath and co-workers for BPA-containing polyphosphonates.¹⁴ In a typical solution polymerization, a 0.15 M dichloromethane solution of BHDB (1 equiv), anhydrous triethylamine (2.5 equiv), and (4-dimethylamino)pyridine (DMAP, catalytic amount) were stirred at -5 °C. To this solution was added a dichloromethane solution of PPDC (1 equiv), and the mixture was allowed to warm to room temperature, where it was stirred for 30 min. As the polycondensation reached high conversion, phenol or 2,6-dimethylphenol was added as an end-capping agent (Table 2). The reaction mixture was then washed with water, and precipitated into cold hexane, to give the BHDB-containing polyphosphonate as a white solid in ~80% isolated yield. GPC estimated the polyphosphonates prepared by solution polycondensation to have molecular weights in the range of ~50 000–150 000 g/mol. The use of DMAP as an acylation catalyst proved beneficial, and the end-capping agents effectively converted labile R-P(O)-Cl chain ends into more stable R-P(O)-OPh groups. The higher molecular weight BHDB-polyphosphonates prepared by solution polymerization were also soluble in many common organic solvents, with spectroscopic features (e.g., ³¹P, ¹H, and ¹³C NMR, and FT-IR) identical to the samples prepared by interfacial polymerization. PCFC studies of these polymers indicated HRC values of ~80–100 J/(g K), in accord with the molecular weight independent nature of this analytical technique for polymer samples. TGA results

(~5% weight loss at 350 °C; ~50% char yield) were also independent of the preparative method. This solution polymerization was run on a 20 g scale without difficulty; higher scale solution polymerizations should be feasible.

In summary, the A₂ bisphenol BHDB is proving to be a versatile monomer in polycondensation chemistry, with potential application to many new polymer materials. The novel polyphosphonates reported here combine the highly desirable property of flame resistance with good solution processability over a range of molecular weights. BHDB as a replacement for BPA is seen to reduce considerably the heat release capacity values of polyphosphonates, and PPDC is an ideal comonomer for lending solubility to such BHDB-containing materials. Further thermal and decomposition studies, as well as mechanical testing, of these novel polyphosphonates are in progress.

Acknowledgment. The authors acknowledge financial support from the members of the antflammable polymers consortium of the Center for UMass-Industry Research on Polymers, including the Federal Aviation Administration, Boeing, General Electric, the International Association of Fire Fighters, Johns Manville, Multina, the National Institute of Standards and Technology, Rogers Corp., Schneller, Solvay Advanced Polymers, and the U.S. Army.

Supporting Information Available: Experimental procedures and spectral data for BHDB-PPDC polyphosphonates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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