

Poly(arylate-phosphonate) Copolymers with Deoxybenzoin in the Backbone: Synthesis, Characterization, and Thermal Properties

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ABSTRACT: Deoxybenzoin-based copolymers containing various relative ratios of arylate and phosphonate units in the backbone were synthesized by solution polycondensation. These copolymers were characterized by gel permeation chromatography, Fourier Transform infrared spectrometry, and proton, carbon, and phosphorous nuclear magnetic resonance spectroscopy (^1H , ^{13}C , and ^{31}P NMR). Pyrolysis combustion flow calorimetry (PCFC) performed on these copolymers revealed their very low heat release capacity, making them attractive for applications in which halogen-free, low flammability materials are desired. Integration of phosphonate units into the polymer backbone is advantageous for achieving high molecular weight polymers with solution processibility while retaining the low flammability inherent to deoxybenzoin-based polymers. Char yields greater than 50% and heat release capacities of 40–60 J/g K, were observed for these copolymers by PCFC. © 2007 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 45: 4573–4580, 2007

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INTRODUCTION

Although synthetic polymers are used extensively in society as plastics, rubbers, and textiles, the flammability of many polymers must be recognized as a safety hazard and an important challenge in polymer research. Flame retardants are incorporated into polymer materials as small molecule additives, or as part of the polymer backbone, to reduce flammability. A number of halogenated molecules, such as brominated aromatics, have been employed to reduce polymer

flammability. Brominated aromatic flame retardants can be found in a wide-range of products, including computers, textiles, foam furniture, and construction materials. The environmental accumulation of halogenated flame retardants raises concerns that are restricting their use, and requires the development of nonhalogenated alternatives.^{1–3} In addition, some halogenated flame retardants release hydrogen halide gas upon combustion,⁴ which is especially undesirable in confined spaces, such as on aircrafts and ships. These concerns have led to an emphasis on nonhalogenated flame retardants in recent years.⁵ Some nonhalogenated flame retardant additives, such as alumina trihydrate, may compromise the physical and mechanical properties of polymers when loaded at high levels.

An ideal low-flammability polymer would be halogen-free and possess high thermal stability,

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low heat of combustion, and a low combustion heat release rate (HRR), with minimal release of toxic fumes. Intrinsically fire-resistant polymers that undergo significant carbonization upon heating are highly desirable, as carbonaceous char formation effectively averts combustion by producing an insulating layer on the polymer surface. Such char formation may also be realized from composite materials in which an additive ultimately provides the desired char.⁶

The HRR of a material has been identified as a key characteristic of polymer flammability.⁷ Several calorimetry methods are available for measuring HRR during combustion, but these methods require relatively large sample quantities (~100 g per experiment) and depend on several factors including ignition source, ventilation, sample thickness, orientation, and edge characteristics.^{8,9} Walters and Lyon developed pyrolysis combustion flow calorimetry (PCFC)^{10–13} as a method to evaluate polymer flammability on very small sample quantities (milligrams). PCFC measures the heat of combustion of the fuel gases that are released by the pyrolysis of a solid in an inert gas stream. The fuel gases then mix with excess oxygen and completely oxidize at high temperature. The instantaneous heat of combustion of the flowing gas stream is then measured by oxygen consumption calorimetry. The heat release capacity (HRC), defined as the maximum amount of heat released per unit mass per degree Kelvin (J/g K), is viewed as an inherent material property and a good predictor of flammability. HRC values obtained by PCFC, across a range of many polymer types, are found to scale with the larger, conventional bench-scale flammability experiments.¹³

Aromatic polyesters prepared from bisphenols and phthalic acids are important high performance engineering thermoplastics.¹⁴ Conventional bisphenol A (BPA)-based polyarylates are well-known and widely used, but exhibit higher-than-desired flammability (e.g., BPA-polyarylates have HRC ~400 J/g K).¹⁵ Polyarylates containing 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (bisphenol C, or BPC) are transparent and processable, and exhibit excellent mechanical and dielectric properties.^{15–18} BPC-based polymers are well within the “ultra fire-resistant” category (HRC < 100 J/g K), with BPC-polyarylates and polycarbonates having reported HRC values of 21 and 29 J/g K, respectively,^{13,19} and high char yields (50–55%). However, the presence of halogen in BPC-based polymers, and the evolution of hydrogen chloride gas at elevated tempera-

tures,^{20,21} may limit their adoption for scale-up and manufacturing as commodity materials.

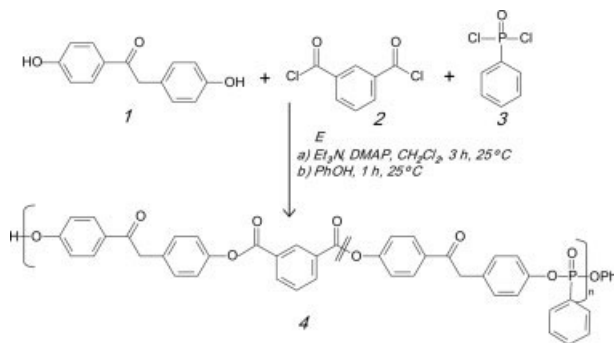
BPC derivatives can be converted to the corresponding diphenylacetylene by loss of the chlorines, followed by phenyl migration.²² In BPC-containing polymers, this reaction represents a viable pathway to char formation,²⁰ in which the presence of chlorine sets up the rearrangement chemistry that leads to diphenylacetylene. In fact, diphenylacetylene-containing poly(aryl ether ketone)s showed heat release characteristics of similar magnitude to the corresponding BPC-versions.²³ However, these alkyne-containing aromatic polymers are prone to side-reactions and crosslinking even at moderately high temperatures,^{24,25} and have less-than-optimal processibility and mechanical properties for many polymer materials applications.

Nonhalogenated, soluble, and thermally stable polymers with diphenylacetylene *precursors* embedded in the backbone might be ideal anti-flammable polymers. In principle, this could be accomplished with deoxybenzoin-based polymers. van der Waals et al. showed the conversion of deoxybenzoins to diphenylacetylenes by flash vacuum pyrolysis at 350–500 °C.²⁶ This report led to our initial synthesis of deoxybenzoin-containing monomers, such as 4,4'-bishydroxydeoxybenzoin (BHDB), and their use in polycondensation chemistry.^{27,28} BHDB-containing polyarylates, prepared from BHDB and isophthaloyl chloride, was found to possess low HRC (~65 J/g K) and high char yield (~45%).²⁷ Moreover, replacing isophthaloyl chloride with phenylphosphonic dichloride (PPDC) gave BHDB-polyphosphonates with better solubility than the BHDB-polyarylate, while maintaining the desired ultralow flammability characteristics (HRC ~80 J/g K; char yield ~50%).²⁸ Here we describe the synthesis and characterization of BHDB-containing copolymers, in which the beneficial features of both the aromatic ester and phosphonate units are integrated into the polymer backbone. For comparative purposes, analogous arylate-phosphonate copolymers based on BPA were synthesized and characterized.

RESULTS AND DISCUSSION

Synthesis and Characterization

Deoxybenzoin-containing poly(arylate-co-phosphonate)s, shown as **4** in Scheme 1, were synthe-



Scheme 1

sized by solution polycondensation of BHDB with isophthaloyl chloride and PPDC at a variety of ratios. The reactions were carried out in anhydrous dichloromethane at room temperature, using triethylamine as base, and 4-*N,N*-dimethylaminopyridine (DMAP) as catalyst. In the late stages of the polymerization, phenol was added to end-cap the polymer, converting the labile P(O)—Cl chain-ends to the more hydrolytically stable P(O)—O—Ph groups.²⁹ Isolated yields of polymer **4**, following precipitation into acetone, ranged from 80 to 95%, and the products were soluble in common organic solvents, such as chloroform, dichloromethane, DMSO, and DMF. Copolymer solubility was found to increase with mole percent phosphonate in the backbone, and gel permeation chromatography (GPC)-estimation of molecular weight (DMF as eluent) generally showed weight-average molecular weights (M_w) over 50 kDa, and polydispersity indices

(PDI) around 2 (Table 1). Higher molecular weights for the phosphonate-containing polymers were always seen relative to the wholly arylate backbone, most likely because of better solubility of the former that prevents termination of the polymerization by precipitation.

The poly(arylate-*co*-phosphonate)s prepared as shown in Scheme 1 were characterized by NMR (¹H, ³¹P, and ¹³C) and FTIR spectroscopy. ¹H NMR spectroscopy on DMSO-*d*₆ solutions of copolymer **4** showed overlapping resonances at 4.3, 4.4, and 4.5 ppm, representing protons of the BHDB methylene group in the copolymer. The multiple signals arise from the different connectivities of BHDB in random copolymers of monomers **1–3**. The signal at 4.3 ppm is assigned to the unit in which BHDB is attached to two phosphonate groups.²⁸ The signal at 4.5 ppm represents the unit in which BHDB is attached to two isophthalate groups,²⁷ whereas that at 4.4 ppm corresponds to the BHDB moiety with phosphonate on one side and isophthalate on the other. ³¹P NMR spectroscopy confirmed the presence of phenylphosphonate in the backbone, with a signal centered at 12.7 ppm. This peak actually consists of three overlapping resonances (12.64, 12.70, and 12.74 ppm), attributed to the three possible connections of the unsymmetrical BHDB about the phenylphosphonate group. In the ¹³C NMR spectrum of polymer **4**, BHDB signals from 196.2–196.4 ppm (carbonyl) and 43.7–43.9 ppm (methylene) were found, as were the remaining expected aromatic and carbonyl resonances. The Fourier Transform infrared spec-

Table 1. Monomer Feed Ratios, Incorporation into Copolymer, Isolated Yields, and GPC-Estimated Molecular Weights for BHDB-Containing Arylate-Phosphonate Copolymers

Isophthaloyl Chloride: PPDC (Molar Ratios)		Yield (%)	GPC ^a		
Feed	Incorporated ^b		M_w (g/mol)	M_n (g/mol)	PDI
100:0	100:0	80	15,100	11,700	1.29
80:20	77:23	88	65,600	37,000	1.78
60:40	57:43	85	50,700	28,500	1.78
50:50	46:54	95	54,600	24,100	2.27
40:60	39:61	92	83,700	31,200	2.69
20:80	23:77	90	61,000	37,000	1.65
0:100	0:100	89	92,700	41,000	2.26

^a GPC performed using DMF as eluent, and molecular weights estimated against polystyrene calibration standards.

^b Calculated by integration of ¹H NMR spectra.

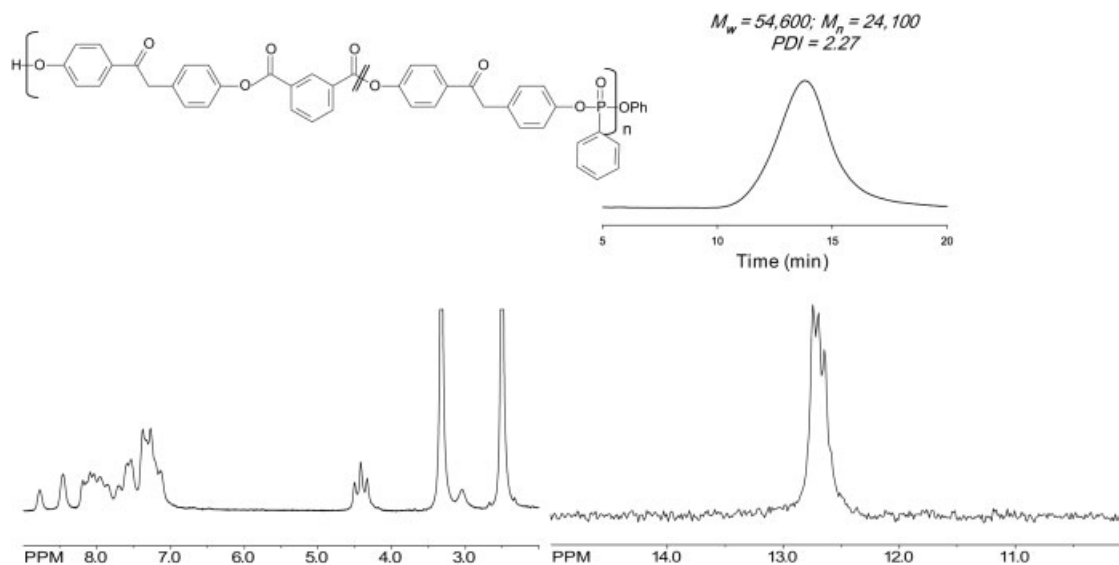


Figure 1. GPC trace (upper right), ^1H NMR spectrum (lower left), and ^{31}P NMR spectrum (lower right) of copolymer **4** (containing $\sim 1:1$ arylate:phosphonate monomer units in the backbone).

trometry (FTIR) spectra of **4** showed strong bands for isophthalate moieties at 1738 cm^{-1} (carbonyl stretching of the ester linkage), phosphonate ($\nu_{\text{P}=\text{O}} = 1272\text{ cm}^{-1}$ and $\nu_{\text{P}-\text{O}-\text{C}} = 1200\text{ cm}^{-1}$), and the deoxybenzoin ketone ($\nu_{\text{C}=\text{O}} = 1683\text{ cm}^{-1}$). Figure 1 shows representative GPC and NMR data from a BHDB-based poly(arylate-*co*-phosphonate) polymer.

Thermal Characterization and Flammability

The flammability characteristics of BHDB-containing poly(arylate-*co*-phosphonate) **4** were examined by PCFC, and the HRC values obtained are reported in Table 2. The HRC of the BHDB-based polyarylate and polyphosphonate

homopolymers were ~ 65 and $\sim 80\text{ J/g K}$, respectively. Interestingly, all of the poly(arylate-*co*-phosphonate) copolymers exhibited even lower HRC values than seen for either homopolymer. The copolymer containing $\sim 4:1$ arylate:phosphonate had a measured HRC of $\sim 50\text{ J/g K}$, whereas the polymers with the lowest HRC values, $\sim 30\text{--}40\text{ J/g K}$, contained a nearly 1:1 arylate:phosphonate ratio. Although this might suggest an optimum monomer ratio for obtaining low flammable polymer materials, all of the copolymers reported in Table 2 exhibit desirably low HRC values.

The BHDB-containing poly(arylate-*co*-phosphonate) copolymers are thermally stable up to $350\text{--}400\text{ }^\circ\text{C}$, at which stage $\sim 5\%$ weight loss is observed by thermogravimetric analysis (TGA).

Table 2. Flammability and Thermal Characterization of BHDB-Copolymers (**4**)

Isophthaloyl Chloride:PPDC (Molar Ratios)	PCFC	TGA		DSC
	Heat Release Capacity (J/g K)	5% Weight Loss Temperature ($^\circ\text{C}$)	Char Yield at $800\text{ }^\circ\text{C}$ (%)	Glass Transition Temperature ($^\circ\text{C}$)
100:0	65 ± 5	340	45	157
77:23	48 ± 4	346	50	142
57:43	41 ± 3	383	56	133
46:54	36 ± 2	367	54	131
39:61	40 ± 3	390	57	124
23:77	59 ± 5	394	55	110
0:100	80 ± 10	397	52	100

All of these copolymers showed high char yield (>50%) at 800 °C (Table 2), with the arylate-phosphonate copolymers having slightly higher char yields than the respective homopolymers (in agreement with the HRC results). The flammability characteristics of the BHDB-copolymers are comparable with that of commercial polyimide (Kapton), an ultrafire resistant material, which exhibited HRC of 25 J/g K and char yield of 52%.¹³

Several phosphorus-based flame retardants, such as aryl phosphates and phosphonates, phosphine oxides, and phosphonic acids are known to promote char through a condensed phase mechanism,^{30–35} whereas some examples show an additional vapor phase activity.³⁶ Phosphorous-based flame retardants undergo thermal oxidative reactions, enhanced by the presence of oxygen-rich polymers, to form phosphoric acid, which catalyzes char formation. At high temperatures, the phosphoric acid is converted to the strongly dehydrating polyphosphoric acid, which can decompose into a polyphosphate glass $[(\text{PO}_3)_n]^{n-}$ coating of the polymer surface, an effective flame barrier.^{30,31}

A condensed phase mechanism that lowers HRC in the phosphorus-containing BHDB-polyphosphonate, relative to the BHDB-polyarylates, appears to be operational here. This effect is exclusive to the BHDB case, as BPA-polyphosphonates actually give lower char yields (~23%) than BPA-polyarylates (~30%).^{27,28} We suggest that the higher oxygen content of BHDB-poly(arylate-co-phosphonate)s, due to the isophthalate and BHDB moieties, is responsible for the highest char yields and lowest HRC values of all the polymers reported here. Moreover, pyrolysis GC/MS of these polymers, which will be detailed in a future manuscript,³⁷ indicated that no phosphorous-containing compounds were present in the volatile decomposition products of BHDB-polyphosphonate. In contrast, BPA-polyphosphonate yielded phosphorus-based volatile products as the major decomposition product.

DSC studies of these BHDB-copolymers revealed glass transition temperatures (T_g) ranging from 100 °C for the BHDB-polyphosphonate to 157 °C for the BHDB-polyarylate (Table 2). These glass transition temperatures were found to be reversible during cooling scans. The BHDB-copolymers, especially those containing ≥ 50 mol % isophthalate units, can potentially be considered for high performance engineering plastics that require low flammability, as these polymers couple relatively high glass transition tempera-

tures (above 130 °C) with their inherently fire-resistant properties.

BPA-Containing Poly(arylate-co-phosphonate)s

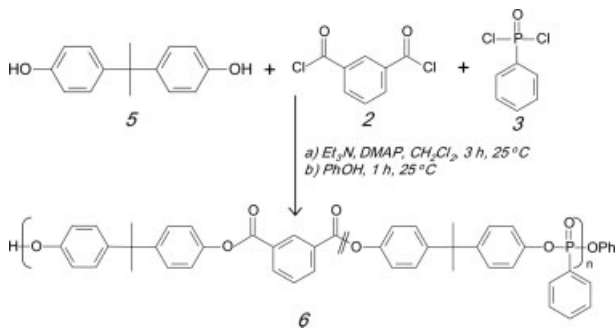
For comparative purposes, the arylate-phosphonate copolymers described previously for BHDB were also prepared by using BPA (Scheme 2) by similar solution polycondensation. Molecular weight, thermal, and flammability data for these polymers are given in Table 3.

PCFC studies of the BPA-based copolymers indicated their moderately high flammability characteristics, with HRC values ranging from 400 to 700 J/g K. Unlike the BHDB case, for the BPA-homopolymers the substitution of isophthalate units with phenylphosphonate led to reduced char yields (< 25%). For the copolymers, the presence of the phosphonate groups led to slightly increased char yield, possibly because of the presence of the oxygen-containing isophthalate in the copolymer backbone. In case of BHDB-copolymers, the presence of both BHDB and isophthalate oxygen-containing units function to increase the char yield and also reduce the HRC values upon incorporation of phosphonate groups. The opposite is seen in the BPA-based copolymers, where higher HRC values are observed.

In future studies, the mechanical properties of BHDB- and BPA-based copolymers containing various comonomer (arylate/phosphonate) ratios will be evaluated to determine the suitability of these polymers in certain materials applications.

SUMMARY

We have reported the synthesis and characterization of novel polyarylate-phosphonate copolymers that are thermally robust, char-promoting,



Scheme 2

Table 3. Properties of BPA–Poly(arylate-co-phosphonate)s (**6**)

Isophthaloyl Chloride:PPDC			GPC ^a			PCFC	TGA	DSC
Feed	Actual ^b	Yield (%)	M_w (g/mol)	M_n (g/mol)	PDI	HRC (J/g K)	Char Yield (%) ^c	T_g (°C)
100:0	100:0	85	137,500	66,800	2.06	385 ± 20	30	183
80:20	77:23	87	113,000	83,000	1.38	415 ± 25	30	160
65:35	67:33	80	173,900	113,200	1.54	595 ± 65	35	133
50:50	53:47	92	143,000	103,000	1.40	710 ± 70	31	137
20:80	26:74	85	82,400	61,400	1.51	480 ± 45	24	116
0:100	0:100	95	73,000	48,500	1.51	440 ± 25	23	115

^a GPC was performed using DMF as eluent, and molecular weights were estimated against polystyrene standards.

^b Calculated by integration of ¹H NMR spectra.

^c At 800 °C.

and low-flammable materials. The polymers were prepared by solution polycondensation of BHDB with different ratios of isophthaloyl chloride and PPDC. The flammability and thermal characteristics of these BHDB-based copolymers were determined by PCFC, TGA, and DSC studies. The presence of phosphonate units in the polymer backbone serves to improve solubility over arylate homopolymers, and also promote char formation and low HRC. These results suggest BHDB-based copolymers as potentially useful high-performance polymers in applications where low flammability is required.

EXPERIMENTAL

Materials

BHDB was prepared from desoxyanisoin.²⁷ BPA, 4-dimethylaminopyridine, and isophthaloyl chloride were purchased from Sigma-Aldrich and used as received. PPDC was purchased from Acros and purified by vacuum distillation. Dichloromethane was washed with sulfuric acid and distilled over calcium hydride. Triethylamine was dried and distilled over calcium hydride.

Characterization

The ¹H, ¹³C, and ³¹P{¹H} NMR spectra were recorded using Bruker Avance400 spectrometer operating at the appropriate frequencies using either residual DMSO as internal reference (¹H and ¹³C) or 85% H₃PO₄ as external reference (³¹P). Infrared spectra were obtained on a Perkin-Elmer Spectrum One FTIR spectrometer equipped with an ATR accessory. Molecular

weights and PDIs were measured by GPC in DMF relative to polystyrene standards on systems equipped with two-column sets (Polymer Laboratories) and refractive-index detectors (HP 1047A) at 50 °C with a flow rate of 1 mL/min. HRC was measured using PCFC, taking the average from three experiments. Samples between 1 and 5 mg were pyrolyzed in nitrogen to 900 °C at a rate of 1 °C/s, followed by complete combustion at 900 °C. Thermogravimetric analysis (TGA) was performed in nitrogen atmosphere on a DuPont TGA 2950 using a ramp rate of 10 °C/min. Glass transition temperature (T_g) data was collected during the second heating from room temperature. Differential scanning calorimetry (DSC) measurements were performed on a DuPont Instruments DSC 2910 at a scan rate of 10 °C/min under a flow of nitrogen (50 mL/min).

Synthesis of BHDB–Poly(arylate-co-phosphonate) **4**

In a dry round-bottom flask equipped with an addition funnel and mechanical stirrer was added a solution of BHDB (1.0 g, 4.4 mmol) in anhydrous dichloromethane (16 mL) and anhydrous triethylamine (1.5 mL, 1.1 g, 11 mmol). To this was added DMAP (15 mg, 0.01 mmol), and the flask was cooled to –5 °C using an ice/ethanol bath. A solution of PPDC (0.60 mL, 2.2 mmol) and isophthaloyl chloride (0.45 g, 2.2 mmol) in anhydrous dichloromethane (10 mL) was added dropwise by addition funnel to the vigorously stirring reaction mixture over 5 min. The reaction mixture was then allowed to warm to room temperature and stirred there for 3 h. Phenol (45 mg, 0.5 mmol) was added, and stirring was continued for 1 h. Then, the reaction mixture was diluted with dichloromethane (250 mL),

REFERENCES AND NOTES

washed with cold water (5×40 mL), dried over anhydrous magnesium sulfate, concentrated to a volume of about 20 mL, and precipitated into a stirred solution of cold acetone (~ 500 mL) to get white fibrous solid. The solid was filtered, washed with acetone, and dried in a vacuum oven at 60°C to give 1.45 g of a white solid (95% yield).

FTIR (powder, cm^{-1}): 1738 ($\nu_{\text{C=O(O)}}$), 1683 ($\nu_{\text{C=O}}$), 1443 ($\nu_{\text{P-C}}$), 1272 ($\nu_{\text{P=O}}$), 1200 ($\nu_{\text{P-O-C}}$). ^{31}P { ^1H } NMR (121 MHz, $\text{DMSO-}d_6$, ppm): δ 12.64 (s), 12.70 (s), 12.74 (s). ^1H NMR (400 MHz, $\text{DMSO-}d_6$, ppm): δ 4.33, 4.42, 4.50 (s, 2H), 7.1–7.38 (m, 6H), 7.56 (m, 2H), 7.72 (m, 1H), 7.95 (m, 4H), 8.45 (m, 2H), 8.8 (m, 1H). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$, ppm): δ 43.7, 43.8, 43.9, 120.2, 121.3, 122.4, 123.1, 127.8, 128.2, 128.5, 130.9, 131.5, 132.9, 133.2, 134.9, 136.2, 148.3, 149.9, 154.3, 154.9, 163.4, 164.5, 196.2, 196.3, 196.4 ppm.

Synthesis of BPA–Poly(arylate-co-phosphonate) 6

Polymer **6** was prepared as described for **4**, using BPA (1.0 g, 4.4 mmol), triethylamine (1.5 mL, 11 mmol), DMAP (15 mg, 0.01 mmol), PPDC (0.60 mL, 2.2 mmol), and isophthaloyl chloride (0.45 g, 2.2 mmol) in anhydrous dichloromethane (25 mL). The dichloromethane solution of the polymer, after washing with water, was precipitated into a stirred solution of cold hexane to afford 1.4 g of a white fibrous solid (92% yield).

FTIR (powder, cm^{-1}): 1739 ($\nu_{\text{C=O(O)}}$), ($\nu_{\text{P-C}}$), 1297 ($\nu_{\text{P=O}}$), 1194 ($\nu_{\text{P-O-C}}$) cm^{-1} . ^{31}P { ^1H } NMR (162 MHz, CDCl_3 , ppm): δ 12.5 (s). ^1H NMR (400 MHz, CDCl_3 , ppm): δ 1.58, 1.66, 1.74 (s, 6H), 7.09 (m, 6H), 7.16 (m, 5H), 7.25 (m, 3H), 7.34 (m, 2H), 7.50 (m, 2H), 7.59 (m, 1H), 7.67 (m, 1H), 7.96 (m, 2H), 8.45 (m, 2H), 9.0 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): 30.9, 30.95, 31.0, 42.3, 42.5, 42.6, 120.0, 121.0, 127.9, 128.1, 128.6, 128.7, 130.4, 132.3, 133.2, 134.9, 147.1, 148.2, 148.6, 148.7, 164.3.

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