

Synthetic and Thermal Studies of Bisphenol-C containing Poly(aryletherketone)s

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Summary

Poly(aryletherketone)s containing 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethene (BPC) were synthesized by the cesium fluoride initiated polymerization of 1,1-dichloro-2,2-bis(4-*t*-butyldimethylsiloxyphenyl)ethane with 4,4'-difluorobenzophenone (**BP-F**). These polymers exhibit high char yields by thermogravimetric analysis (TGA), and low heat release capacities were measured by pyrolysis combustion flow calorimetry (PCFC). Poly(aryletherketone)s were prepared from **BP-F** and various ratios of BPC and bisphenol-A (BPA), and their thermal properties characterized by TGA and PCFC.

Introduction

As the organic nature of many polymer materials imparts high flammability, a great deal of research has been devoted towards improving their fire-resistance. Much of this work has involved the addition of small molecule flame-retardants to commercially available polymers. As an alternative to this “filler” approach, there is significant interest in the development of new thermoplastics that are inherently fire-resistant without the need for small molecule additives. Current research activities on such “fire-safe” polymers is multifaceted [1-6] and includes but is not limited to 1) the preparation of novel polymers with exceedingly good flame-resistance and low heat release upon burning; 2) polymers that combine the relevant thermal properties with good processability to allow film and fiber formation; 3) the production of “fire-safe” polymers with limited halogen content to lower the environmental impact; and 4) a mechanistic understanding of the energetic processes (e.g., bond-forming and breaking steps) associated with burning organic polymer molecules.

High-performance polymers such as polyetheretherketones (PEEK), polyetherketones (PEK), and polyethersulfones are well known for their high thermal stabilities and fire-resistant properties that are among the best of any commercial polymers [1,2]. Nevertheless, improvements are needed before these polymers will meet the stringent requirements mandated by many governmental organizations [1,2]. We are interested in the preparation of novel poly(aryletherketone)s that include flame-retardant moieties within the polymer structure and still maintain the advantageous material properties of PEEK and PEK.

1,1-Dichloro-2,2-bis(4-hydroxyphenyl)ethene, commonly referred to as "bisphenol-C" (BPC), has been acknowledged as a prime candidate for providing flame-resistance to polymeric materials [5,6]. Materials containing BPC in the backbone possess fire-resistant properties due to their high char-yields and release of hydrogen chloride gas [5,6], an effective combustion inhibitor [7]. From an environmental standpoint, it should be noted that the halogen content in BPC is lower than that of the highly halogenated aromatic molecules and polymers that represent environmental hazards. Herein we report the synthesis and thermal characterization of BPC-containing poly(aryletherketone)s with chemical structures similar to PEEK and PEK.

BPC-poly(aryletherketone)s were first reported by General Electric, Inc. in the 1970's [8] through the polycondensation of chloral with diphenyl ether, followed by dehydrochlorination to give 1,1-dichloro-2,2-diphenyl ethene in the polymer backbone. This polymer was reported to possess a high limiting oxygen index (LOI) and to be "self-extinguishing" upon ignition. However, electrophilic aromatic substitutions of this type give mixtures of *ortho*- and *para*- substitution [9], and the reported method requires post-polymerization transformations. We sought to synthesize BPC containing poly(aryletherketone)s by a nucleophilic approach to provide a more precise structure and to allow for the controlled synthesis of copolymers with tunable BPC content.

Experimental

Materials

1,1-Dichloro-2,2-bis(4-hydroxyphenyl)ethene was provided by Eikos, Inc. *t*-Butyldimethylsilyl chloride and 4,4'-difluorobenzophenone were purchased from Alfa Aesar, and bisphenol-A was provided by Allied Signal. Imidazole, cesium fluoride, and *N*-methylpyrrolidone were purchased from Sigma-Aldrich. 2,2-Bis(4-*t*-butyldimethylsiloxyphenyl)propane was synthesized according to a literature procedure [10]. 4,4'-Difluorobenzophenone was recrystallized from methanol. Cesium fluoride was crushed into fine particles and dried at 110 °C. *N*-methylpyrrolidone was purified by azeotropic distillation with benzene and then distilled under vacuum. Methylene chloride was distilled over calcium hydride.

Instruments

NMR spectra were recorded on CDCl₃ solutions using a Bruker DPX-300 spectrometer unless otherwise noted: ¹H at 300 MHz and ¹³C at 75 MHz, referenced to residual CHCl₃. Molecular weights were estimated by gel permeation chromatography (GPC) in THF relative to polystyrene standards (Scientific Polymer Products peak-average molecular weight (*M_p*); 503, 700, 1306, 2300, 4760, 12,400, 196,700, and 556,000 g/mol) on a system equipped with a three-column set (Polymer Laboratories 300; 7.5 mm, 2 Mixed-D, 50) and a refractive-index detector (Waters R4010). Thermal gravimetric analysis was performed in a nitrogen atmosphere on a DuPont TGA 2950 and TGA 2050 using a ramp rate of 10°C. Glass transition temperatures (*T_g*) were recorded under a nitrogen atmosphere on the second run using a DuPont DSC 2910 differential scanning calorimeter with a ramp rate of 10°C/min. Heat release capacity and total heat release were measured using pyrolysis combustion flow calorimetry (PCFC) [11-14] where the average of five samples of 1.0 ± 0.1 mg were pyrolyzed in nitrogen from 350 °C to 930 °C at a heating rate of 4.3 °C/s using a

Pyroprobe 2000 and then completely combusted at 900 °C. Intrinsic viscosities were measured at 25 °C in chloroform with a Ubbelohde viscometer.

*Synthesis of 1,1-dichloro-2,2-bis(4-*t*-butyldimethylsiloxyphenyl)ethane (BPC-Si)*

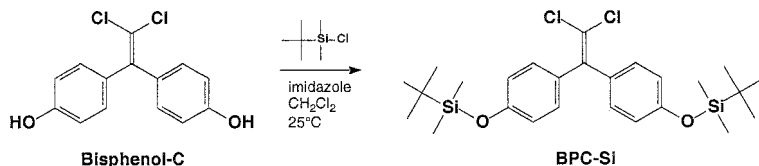
1,1-Dichloro-2,2-bis(4-hydroxyphenyl)ethene (10.0 g, 47.8 mmol), *t*-butyldimethylsilyl chloride (15.0 g, 106 mmol), imidazole (13.5 g, 144 mmol) and methylene chloride (100 mL) were added to a round bottom flask. The slurry was stirred at room temperature for 12 hours under nitrogen. The resulting mixture was extracted twice with water and once with brine. The organic layer was dried over MgSO₄, filtered and concentrated by rotary evaporation to give a brown oil. This oil was eluted through silica gel in hexane/ethyl acetate with a mixture of 5% ethyl acetate in hexanes to afford white crystals (12.0 g, 55%): mp 90 °C; ¹H NMR δ 7.13 (d, 4H, J=8.7 Hz), 6.77 (d, 4H, J=8.7 Hz), 0.97 (s, 18H), 0.20 (s, 12H) ppm; ¹³C NMR δ 155.3, 139.9, 132.6, 130.8, 119.5, 117.6, 25.6, 4.4 ppm. Fourier transform infrared ν 3038 (C-H aromatic, w), 2957, 2930, 2888, 2850 (C-H aliphatic, m), 1604 (Cl₂C=C, s), 1569 (C=C aromatic, w), 1509 (C=C aromatic, s), 1472 (C=C aromatic, m), 1464 (C=C aromatic, w), 1258 (Si-O, s) cm⁻¹.

Polymerization procedure

To a round bottom flask equipped with a magnetic stirbar was added **BPC-Si** (0.63 g, 1.8 mmol), 4,4'-difluorobenzophenone (0.27 g, 1.8 mmol), cesium fluoride (30 mg), and *N*-methylpyrrolidone (3 mL). The flask was capped with a septum and placed into a preheated oil bath (150 °C) while stirring under an argon atmosphere. Within 5 minutes, the clear solution appeared dark-brown. After 12 hours, the flask was removed from the oil bath and methylene chloride (2 mL) was added. The solution was added dropwise to methanol (60 mL). The resulting solid was filtered and dried under vacuum to give an off-white powder (0.60 g, 75%): ¹H NMR (600 MHz on a Bruker Avance 600) δ 7.80(d, 4H, J=4.0 Hz), 7.30(d, 4H, J=4.0 Hz), 7.06(d, 4H J=4.7 Hz), 7.04(d, 4H J=4.3) ppm; ¹³C NMR δ 194.0, 160.56, 155.7, 138.9, 135.2, 132.7, 132.2, 131.2, 119.3, 117.9, 115.6, 115.3, 115.2 ppm. Anal. calcd for C₂₇H₁₆Cl₂O₃: C 70.60%; H 3.51%; Cl 15.44%; Found: C 70.20%; H 3.24%, Cl 14.42%. This procedure is also representative for copolymers of **BPC-Si**, **BPA-Si** and **BP-F**.

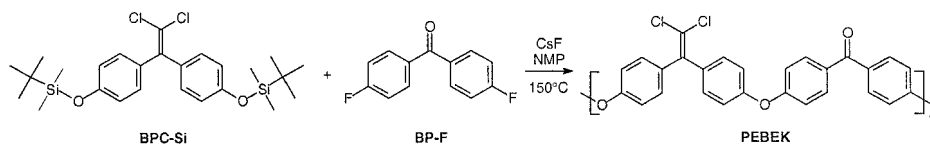
Results and Discussion

The synthesis of poly(aryletherketone)s using bisphenol-A (BPA) has been reported by Kricheldorf for a series of poly(aryletherketone)s and poly(arylethersulfone)s made from silylated BPA [15-20]. Thompson *et al.* synthesized oligomeric aryletherketones from BPA using similar chemistry [21,22]. Based on this precedent and since BPC has been used previously with good success as a replacement for BPA to impart flame-resistance to polycarbonates and polyarylates [5,6], we sought to prepare BPC containing poly(aryletherketone)s by related methods using 1,1-dichloro-2,2-bis(4-*t*-butyldimethylsiloxyphenyl)ethane (**BPC-Si**) as shown in Scheme 1. The TBDMS protecting group was chosen for its excellent stability during purification and later amenability to deprotection and polymerization. [23]



Scheme 1: Preparation of 1,1-dichloro-2,2-bis(4-t-butyldimethylsiloxyphenyl)ethene

The $A_2 + B_2$ polycondensation of **BPC-Si** with 4,4'-difluorobenzophenone (**BP-F**) was initiated with cesium fluoride at 150 °C in *N*-methylpyrrolidone (NMP) as shown in Scheme 2. The high affinity of fluoride ion for silicon results in deprotection of the silyl ethers on **BPC-Si**. The release of TBDMS-fluoride leaves a nucleophilic phenolate available to react with aryl fluorides *via* the Meisenheimer complex [24], whereby elimination of fluoride restores aromaticity and completes the substitution. The resulting polymer, BPC-*co*-benzophenone, or polyether(BPC)etherketone (referred to hereafter as **PEBEK**), was isolated in good yield in moderate to high molecular weights after precipitation into ethanol.



Scheme 2: Polymerization of **BPC-Si** with 4,4'-difluorobenzophenone (**BP-F**).

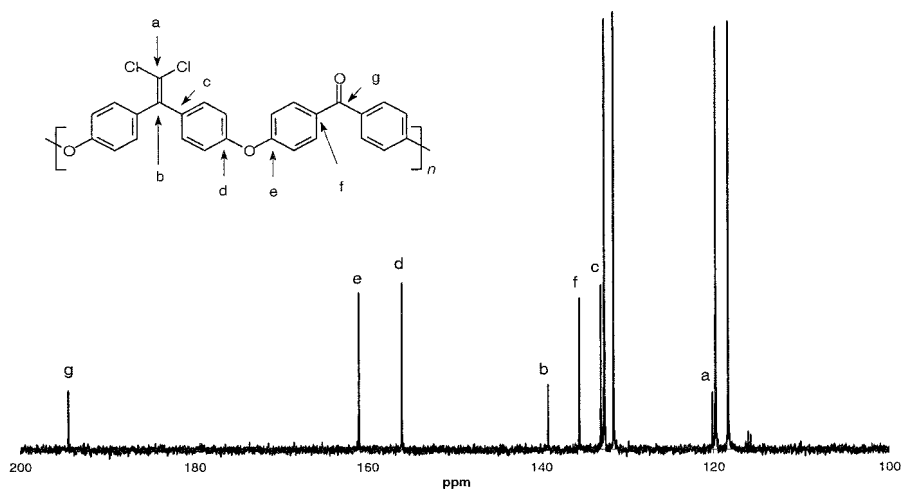


Figure 1: ^{13}C NMR of PEBEK showing peak assignments.

The use of NMP was crucial for solubilization of the phenolate of BPC and thus for successful polymerization. In addition, polymerizations performed under argon

produced more consistent results than those performed under nitrogen; trace levels of water and/or oxygen may inhibit polymerization. These BPC-polyethers are soluble in common organic solvents (e.g., >500 mg/mL in tetrahydrofuran, methylene chloride, and chloroform) and produce free standing films upon solution casting onto glass slides.

Proton and carbon-13 NMR measurements are consistent with the expected incorporation of both monomers into the polymer backbone. The ^{13}C NMR of PEBEK is shown in Figure 1. Resonances denoted by a and b in Figure 1 indicate that the flame-retardant moiety (1,1-dichloro-2,2-diphenylethene) is retained within the polymeric structure. Resonance g shows that the ketone provided by the monomer **BP-F** has remained intact. Resonances near δ 115 ppm are believed to result from phenolic endgroups as they are consistent with the phenolic resonances of BPC.

Table 1: Synthetic results for copolymers of BPA-Si and BPA-Si with BP-F.

Polymer	BPA-Si (mol %) ^a	BPC-Si (mol %) ^a	BPA (mol %) ^b	BPC (mol %) ^b	M_n	M_w	PDI	$[\eta]$ (dL/g)
PEBEK	0	100	0	100	17000	118000	7.0	0.42
1	25	75	23	77	9900	24200	2.4	0.23
2	50	50	47	53	18000	69400	3.9	0.41
3	60	40	54	46	13000	72300	5.6	0.50
4	70	30	67	33	16500	122000	7.4	0.66
5	75	25	69	31	17900	187000	10.4	0.84
6	100	0	100	0	16600	46600	2.8	0.46

^a Monomer Feed Ratio.

^b Incorporation into polymer as calculated from proton NMR integrations assuming one BP unit per bisphenol.

To evaluate the effect of BPC as a flame-retardant in these materials, we synthesized a series of copolymers in which **BPC-Si** and 2,2-bis(4-*t*-butyldimethylsiloxyphenyl)propane (**BPA-Si**) were varied over a range of ratios. Increased levels of BPC in the polymer product might be expected to lead to an increased fire-resistance. The synthetic procedure used to make these copolymers is identical to that of **PEBEK**. Table 1 lists the various feed ratios used to produce these copolymers and the level of incorporation of these monomers into the polymeric structure as determined by integration of proton NMR. The mol % of each monomer within the polymer matches the feed ratios reasonably well. Molar masses for these polymers were determined by GPC and are also reported in Table 1 [25].

Table 2: Thermal analysis for copolymers of BPC-Si and BPA-Si with BP-F.

Polymer	Char Yield ^a at 900°C (%)	HR Capacity (J/g·K)	Total HR (kJ/g)	T_g (°C)
PEBEK	59	30	6.2	137
1	58	38	6.9	137
2	57	90	9.1	158
3	59	90	9.0	159
4	51	133	10.4	155
5	46	126	11.2	157
6	42	238	14.5	149

^a Char yield determined by TGA

As shown in Table 2 and Figure 2a, increasing the BPC content results in increased char yields up to about 50-60 mol % of BPC incorporation (relative to total phenol content). At this mol %, the char yield reaches a plateau at 57-59%, and does not

increase with higher BPC content. This result demonstrates the maximum amount of halogen needed to impart the desired fire-resistant properties. High char yields are considered crucial in reducing polymeric flammability as less material is released into the vapor phase and made available for combustion [1-6]. Further, while halogenated materials are generally considered to act in the vapor phase to impart flame-retardancy [4], in BPC containing materials, promotion of condensed phase charring appears to be the primary flame-retardant activity of the halogen [5,6]. Work is ongoing to determine the mechanism of this char formation [29].

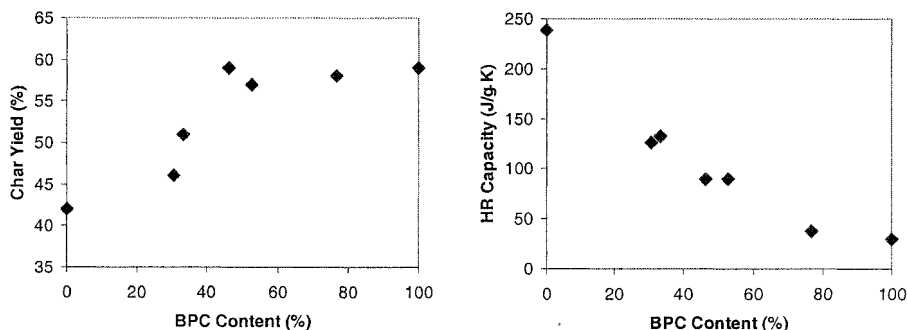


Figure 2: (a) Char yield increases until it plateaus at ~50 mol % (left). (b) HR capacity decreases with increasing BPC content (right).

These polymers were also analyzed using a pyrolysis combustion flow calorimeter (PCFC) designed specifically for the purpose of fire-resistance screening of small quantities of materials (~1 mg) [11-14]. PCFC measures the total heat released (THR), a measure of the total amount of energy evolved during the pyrolysis of a given material, and the heat release (HR) capacity, a measure of the greatest instantaneous release of energy. Heat release capacity has been identified as a key parameter in determining fire-resistance [2,4,11-14]. As shown in Table 2 and Figure 2b, the HR capacity decreases with increasing BPC-Si.

This can be explained through analysis of the TGA curves (Figure 3) for these copolymers. Heat release rates are proportional to the rate of mass loss, which is represented by the steepness of the TGA curves during decomposition. Faster mass loss rates result in greater quantities of volatiles released at a given instant, which in turn results in greater energy release rates during combustion. From a materials “fire-safe” perspective, it is beneficial for decomposition to occur over a wide temperature range. As shown in Figure 3, **PEBEK** decomposes over a much broader temperature range than copolymer **6**, the polymer containing no BPC. Copolymer **3**, inclusive of both BPC and BPA units, has a TGA curve that closely resembles that of **PEBEK**, and hence its HR capacity is much less than that of **3**. Charring plays a key role in reducing HR capacity in that a lower quantity of volatile material is released. Thus the copolymers with higher char yields have reduced HR capacities.

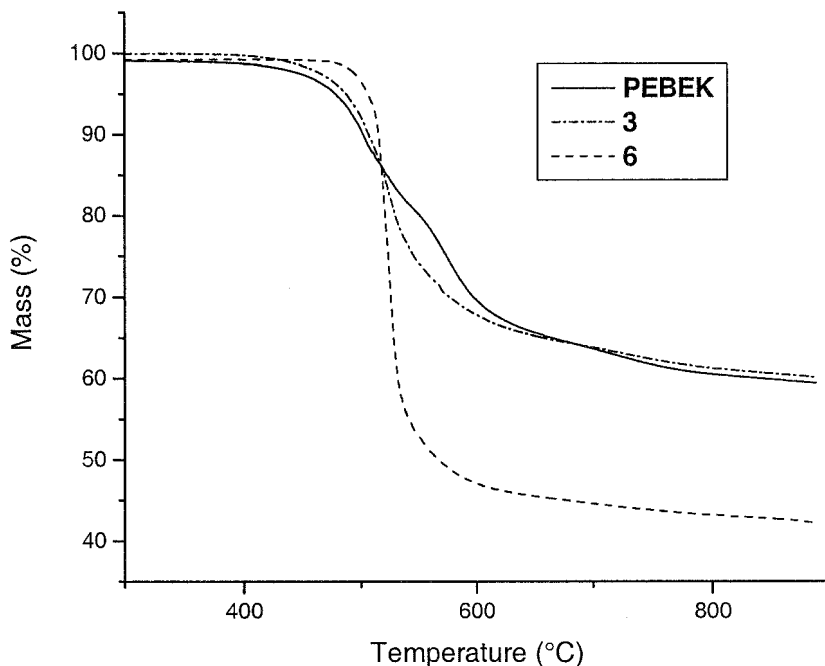


Figure 3: TGA curves for **PEBEK**, **3**, and **6** showing mass loss rate decreasing with increasing BPC content (see text).

In summary, we have shown the synthesis of polyether(BPC)etherketone through the polymerization of silylated bisphenol-C with 4,4'-difluorobenzophenone. This material exhibits excellent fire-resistant properties as shown by TGA and PCFC. Furthermore, copolymers of varying composition have been synthesized using a combination of bisphenol-C and bisphenol-A. Analysis of these copolymers reveals that fire-resistant properties diminish when the bisphenol-C content is decreased to about 40-50 mol%. This may represent a suitable target for BPC-content in materials where fire-resistance is needed. We believe that the versatility and ease of synthesis of these BPC-containing polymers make them viable candidates for use in many different types of materials applications, and further work will be performed in this regard.

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25. The high PDI values of some of the polymer samples may be due to small amounts of crosslinking that occur through the BPC functionality. There have been reports that polymers containing 1,1-dichloro-2,2-diphenyl moieties crosslink upon heating [26-28]. We have observed that these polymerizations will undergo gelation (and cannot be dissolved) if the reaction proceeds at high temperatures for over approximately 12-15 hrs. The addition of the radical scavenger 2,6-di-*t*-butyl-4-methylphenol helps reduce this effect.
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