



# Soluble, semi-crystalline PEEK analogs based on 3,5-difluorobenzophenone: Synthesis and characterization

Andria Fortney, Eric Fossum\*

Department of Chemistry, Wright State University, 202 Oelman Hall, 3640 Colonel Glenn Highway, Dayton, OH 45435, USA

## ARTICLE INFO

### Article history:

Received 12 January 2012

Received in revised form

22 March 2012

Accepted 24 March 2012

Available online 3 April 2012

### Keywords:

Poly(arylene ether)s

Copolymer

Crystallinity

## ABSTRACT

The solubility and thermal properties of poly(ether ether ketone) (PEEK) have been modified by utilizing various ratios of the traditional electrophilic component, 4,4'-difluorobenzophenone, **1**, utilized to synthesize PEEK and a comonomer, 3,5-difluorobenzophenone, **2**, which is simply a geometric isomer of **1**. The resulting polymers ("m-PEEK") have the same chemical composition as PEEK, allowing for accurate structure–property relationships to be determined. The thermal properties were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The ratio of monomer **1** to monomer **2** had a dramatic influence on the thermal properties and solubility characteristics of PEEK. At higher ratios, 90:10, 85:15, and 80:20, the materials were semi-crystalline and their solubility was very limited in solvents such as *N*-methyl-pyrrolidinone (NMP) while at lower ratios, 75:25 and 50:50, the PEEK derivatives were completely amorphous and soluble in NMP. TGA analysis indicated excellent thermal stability as most of the materials displayed 5% weight loss temperatures ( $T_{d-5\%}$ ) greater than 450 °C.

© 2012 Elsevier Ltd. All rights reserved.

## 1. Introduction

Due to their excellent mix of properties poly(arylene ether)s, PAEs, are widely used as engineering thermoplastics [1,2]. Poly(ether ether ketone), PEEK, is a semi-crystalline polymer consisting of *para* linked phenyl and benzophenone units (Fig. 1) [3–5]. PEEK's structure and its semi-crystalline nature provide excellent mechanical properties, thermooxidative stability, and solvent resistance, however, its solubility is generally limited to harsh solvents such as concentrated sulfuric acid. Thus, the processing of PEEK can be somewhat challenging. A number of methods have been developed to enhance the solubility and processability of PEEK including: (1) introduction of functional groups [6–10], (2) incorporation of comonomers [11–13], (3) disrupting the symmetry by introducing *meta* or *ortho* linked monomer units [4,14–17], and (4) increasing the number of ether bonds per repeat unit [18].

The synthesis of PEEK is typically achieved via the nucleophilic aromatic substitution (NAS) reaction of hydroquinone with 4,4'-difluorobenzophenone, **1** [3,5,19]. The reaction is carried out at extremely high temperatures in order to overcome the solubility difficulties associated with the resulting polymer. Recently, we have

developed NAS reactions that involve displacement of aryl fluorides, which are activated by the presence of strong electron withdrawing groups located in the *meta* position [20–22]. The end result is a PAE in which the NAS activating group is present as a pendant moiety, rather than being directly incorporated into the backbone. Essentially, the geometric isomers of many of the more common PAEs can be prepared as long as the corresponding 3,5-difluoro aromatic systems are available. For example, a PEEK-like derivative was prepared from 3,5-difluorobenzophenone, **2**, and bis-(4-hydroxyphenyl) ether (*m*-PEEEK) [21], which is the geometric isomer of poly(ether ether ether ketone), PEEK (Fig. 1) [18]. While PEEK is semi-crystalline, the polymer prepared with 3,5-difluorobenzophenone was completely amorphous.

This paper describes efforts to prepare a geometric isomer of the more well known PEEK and subsequently tailor the crystallinity and solubility properties by preparing copolymers with varying ratios of 4,4'-difluorobenzophenone and 3,5-difluorobenzophenone. The ultimate goal was to prepare a geometric isomer of PEEK that was soluble in common organic solvents while maintaining a high level of crystallinity, but also possessed a site for relatively straightforward functionalization. For discussion purposes we will refer to what is essentially the homopolymer of hydroquinone and 3,5-difluorobenzophenone as *meta*-PEEK (*m*-PEEK, Fig. 1) although it is really an alternating copolymer of 1,3 and 1,4 poly(phenylene oxide) bearing a pendant benzoyl group at the 5 position of each 1,3

\* Corresponding author.

E-mail address: [eric.fossum@wright.edu](mailto:eric.fossum@wright.edu) (E. Fossum).

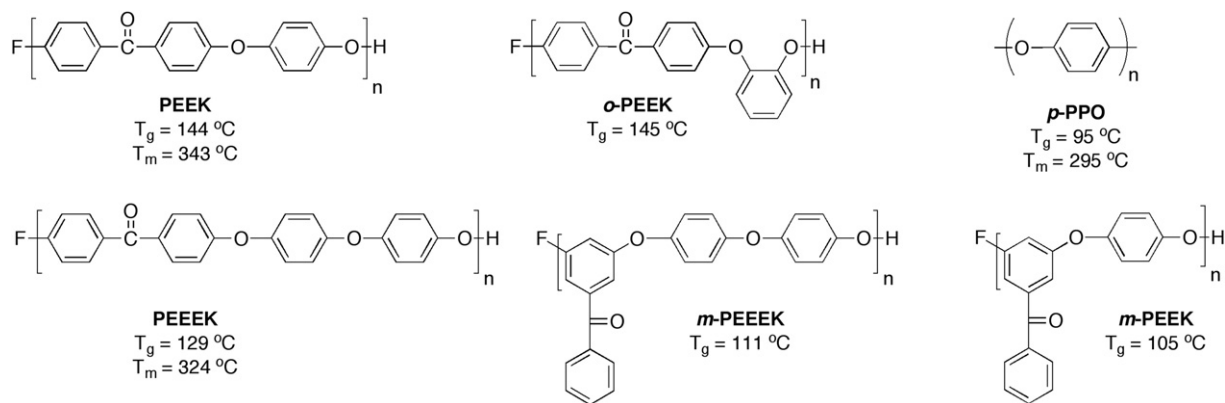


Fig. 1. Structures of PEEK, PEEK, o-PEEK, m-PEEEK, PPO, and m-PEEK.

phenyl ring. In order to avoid the synthetic challenges associated with using hydroquinone as the bisphenol component, such as cyclization and oxidation issues, two isomeric forms of an oligomeric bisphenol were utilized, 4,4'-bis(4-hydroxyphenoxy)benzophenone, **3** [23], and 3,5-bis(4-hydroxyphenoxy)benzophenone, **4**. The structure–property relationships of the resulting polymers were evaluated through a combination of thermal analysis, solubility, and X-ray diffraction studies.

## 2. Experimental

### 2.1. Materials

All reactions were performed under a nitrogen atmosphere and all transfers were done using syringes or cannula as necessary. *N*-methyl-pyrrolidinone, (NMP), HPLC grade (Sigma–Aldrich) was dried over  $\text{CaH}_2$  and distilled under a nitrogen atmosphere prior to use. Tetrahydrofuran (THF), ACS grade (VWR), was used as received. 3,5-Difluorobenzophenone, **2**, was purchased from Alfa Aesar and recrystallized from ethanol prior to use. 4,4'-difluorobenzophenone, **1**, was purchased from Oakwood Products, Inc. Hydrobromic acid (40%) and *p*-methoxyphenol were purchased from Sigma Aldrich and used as received. 4,4'-Bis-(4-hydroxyphenoxy)benzophenone, **3**, was prepared according to a literature procedure [23].

### 2.2. Instrumentation

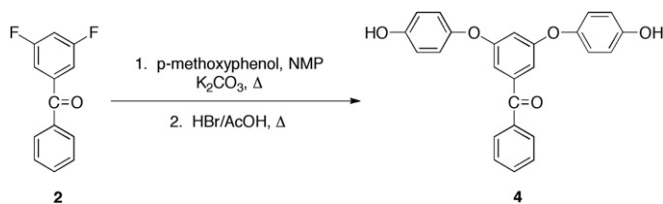
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained using a Bruker AVANCE 300 MHz instrument operating at 300 and 75.5 MHz, respectively. Samples were dissolved in (dimethylsulfoxide)- $d_6$  or chloroform- $d$  as required. Size Exclusion Chromatography (SEC) analysis was performed using a system consisting of a Viscotek Model 270 Dual Detector (viscometer and light scattering) and a Viscotek Model VE3580 refractive index detector. Two Polymer Laboratories 5 mm PL gel Mixed C columns (heated to  $40\text{ }^{\circ}\text{C}$ ) were used with tetrahydrofuran as the eluent and a Thermoseparation Model P1000 pump operating at 1.0 mL/min. Weight average molecular weights,  $M_w$ , were determined using the SEC light scattering detector while the polydispersity indices were calculated from the RI signal. Differential Scanning Calorimetry (DSC) analyses were performed under nitrogen on a TA Instruments Q200 DSC while Thermogravimetric (TGA) analyses were performed under nitrogen and air atmospheres on a TA Instruments Q500 TGA, at a heating rate of  $20\text{ }^{\circ}\text{C}/\text{min}$ . X-Ray diffraction data were acquired using a Rigaku Miniflex II Desktop X-Ray Diffractometer measured from an angle ( $2\theta$ ) range of  $10^{\circ}$ – $90^{\circ}$ .

### 2.3. 3,5-Bis-(4-hydroxyphenoxy)benzophenone, **4**

In a 50 mL RB flask, equipped with a stir bar, Dean–Stark trap, a condenser, and  $\text{N}_2$  gas outlet, were placed 2.0 g (9.1 mmol) of 3,5-difluorobenzophenone, 3.41 g (27.5 mmol) of 4-methoxyphenol and 5.7 g (41.2 mmol) of  $\text{K}_2\text{CO}_3$  along with 10 mL of toluene and 14 mL of NMP. The Dean–Stark trap was filled with toluene and the mixture was heated to  $150\text{ }^{\circ}\text{C}$  for approximately 4 h to ensure complete dryness. The toluene was removed and the reaction temperature was raised to  $185\text{ }^{\circ}\text{C}$  for an additional 16 h at which point the mixture was cooled to room temperature. The solution was added dropwise, with vigorous stirring, to dilute aqueous HCl (300 mL), pH  $\sim 4$ . The organic material was extracted into 200 mL of toluene. The layers were separated and the organic layer was dried over  $\text{MgSO}_4$  and concentrated under reduced pressure to afford a yellow oil. The oil was then redissolved in 200 mL of toluene and washed ( $5\times$ ) with 200 mL of a saturated sodium carbonate and 300 mL of water ( $2\times$ ). The toluene layer was then dried over  $\text{MgSO}_4$  and concentrated under reduced pressure, yielding a light yellow oil, which was triturated with 200 mL of distilled water at  $90\text{ }^{\circ}\text{C}$  for 6 h, followed by vigorous stirring at room temperature resulting in 3.44 g (88%) of a yellow solid. The crude material was used without any further purification.  $^1\text{H}$  NMR (DMSO- $d_6$   $\delta$ ): 3.76 (s, 6H); 6.80 (t, 1H); 6.83 (d, 2H); 6.99 (d, 4H); 7.10 (d, 4H); 7.52 (t, 2H); 7.66 (m, 1H); 7.72 (m, 2H). GC/MS:  $m/z$ : 426.

In a 500 mL RB flask, equipped with a stir bar, reflux condenser, and  $\text{N}_2$  gas inlet, were placed 3.44 g (8.1 mmol) of 3,5-bis-([*p*-methoxyphenoxy]) benzophenone, 20 mL of 48% hydrobromic acid and 200 mL of glacial acetic acid. The resulting mixture was heated to  $130\text{ }^{\circ}\text{C}$  for 4 days at which point the solution was allowed to cool to room temperature and then poured into 500 mL of vigorously stirred distilled water to afford a light brown semi-solid. The organic material was extracted into 250 mL of chloroform and the layers were separated. The chloroform layer was then washed with 500 mL of saturated sodium bicarbonate ( $2\times$ ) and 500 mL of distilled water, followed by drying over magnesium sulfate. The chloroform was then removed using a rotary evaporator to afford a yellow oil, which was dried further under vacuum affording 2.63 g (82%) of a light pink solid. The crude product was triturated with 50 mL of ethanol:water solution (50:50) leaving behind a yellow oil, which was redissolved in 50 mL of chloroform. The chloroform solution was dried over  $\text{MgSO}_4$  and concentrated under reduced pressure, followed by drying under vacuum to afford 1.47 g (45.7%) of a cream colored solid.

$^1\text{H}$  NMR (DMSO- $d_6$   $\delta$ ): 6.74 (t, 1H); 6.80 (m, 6H); 6.98 (d, 4H); 7.52 (t, 2H); 7.66 (tt, 1H); 7.72 (dd, 2H);  $^{13}\text{C}$  NMR (DMSO- $d_6$   $\delta$ ): 109.0, 110.8, 116.4, 121.4, 128.5, 129.6, 132.9, 136.3, 139.2, 146.7, 154.4, 159.8, 194.5. GC/MS:  $m/z$ : 399.



**Scheme 1.** Synthesis of 3,5-bis(4-hydroxyphenoxy)benzophenone, **4**.

#### 2.4. Synthesis of *m*-PEEK, **5**

In a 25 mL RB flask, equipped with a stir bar, reflux condenser, and N<sub>2</sub> gas inlet, were placed 0.29 g (0.72 mmol) of 3,5-bis-(4-hydroxyphenoxy)benzophenone, **4**, and 0.16 g (0.72 mmol) of 3,5-difluorobenzophenone, **2**, along with 1.1 mL of NMP. The resulting mixture was heated to 185 °C and held there for 48 h. The resulting dark brown solution was then allowed to cool to room temperature, followed by diluting with 3 mL of NMP. The polymer solution was added dropwise to 300 mL of vigorously stirred acidified water (~4 pH) to afford dark brown, fine particulates, which were isolated via filtration and dried under vacuum to afford 0.33 g (75%) of **5** as a dark brown solid. The crude material was redissolved in 4 mL of NMP and precipitated from 250 mL of isopropanol to afford 0.18 g (42%) of a dark tan solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 6.78 (b, 1H); 6.96 (b, 6H); 7.32 (m, 2H); 7.45 (m, 1H) 7.68 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ): 112.0, 113.9, 121.0, 128.6, 130.1, 132.8, 136.8, 140.3, 152.3, 159.0, 195.1.

#### 2.5. P<sub>50</sub>-Alt-*m*-P<sub>50</sub> copolymer using 3,5-bis-(4-hydroxyphenoxy) benzophenone, **6**

The alternating copolymer **6** was prepared according to the same procedure as utilized for the synthesis of *m*-PEEK, except that 4,4'-difluorobenzophenone, **1**, was used in place of **2**.

(45% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 6.83 (t, 1H); 6.95, (d, 4H); 7.01, (b, 10H); 7.38 (t, 2H); 7.50 (t, 1H); 7.71 (bd, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ): 112.0, 113.9, 117.1, 121.0, 128.6, 130.1, 132.2, 132.3, 132.8, 136.8, 140.3, 152.0, 152.3, 159.0, 161.5, 194.0, 195.1.

#### 2.6. General procedure for copolymers **7(a–e)**

As an example procedure the synthesis of P<sub>75</sub>-co-*m*-P<sub>25</sub>, **7b**, will be described. In a 25 mL RB flask, equipped with a stir bar, condenser, and gas inlet were placed 0.40 g (1.0 mmol) of 4,4'-bis(4-hydroxyphenoxy)benzophenone, **3**, 0.11 g (0.50 mmol) of 3,5-difluorobenzophenone, **2**, and 1.8 mL of NMP. The resulting mixture

was stirred at 185 °C for 16 h at which point 0.11 g (0.50 mmol) of 4,4'-difluorobenzophenone were added and the mixture was stirred at 185 °C for an additional 8 h. The resulting dark brown solution was diluted with 4 mL of NMP and heated for 2 h further at 150 °C to ensure a homogeneous solution. The NMP solution was then cooled to room temperature and added dropwise to 200 mL of vigorously stirred distilled water to afford a light tan solid which was isolated via filtration, followed by drying under vacuum. The product was redissolved in NMP and reprecipitated twice, first using distilled water and finally from isopropanol:water (95:5) to provide a light tan colored solid, which was isolated via filtration and dried under vacuum to afford 0.46 g (75%) of an off white solid.

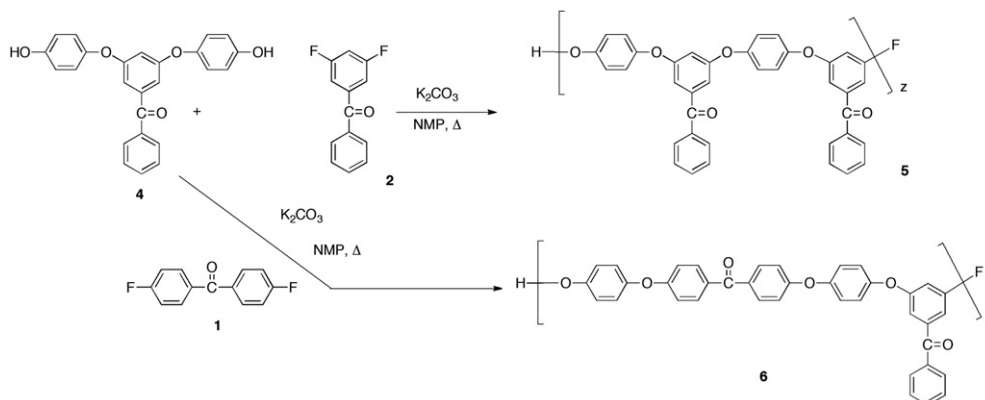
### 3. Results and discussion

#### 3.1. Polymer synthesis

Initial attempts to prepare *m*-PEEK via the reaction of hydroquinone and 3,5-difluorobenzophenone, **2**, resulted in the formation of only relatively low molecular weight materials, which included a high percentage of cyclic species. In order to overcome this apparent limitation in the synthesis of *m*-PEEK, an oligomeric bisphenol species, 3,5-bis(4-hydroxyphenoxy)benzophenone, **4**, was prepared according to the procedure outlined in Scheme 1. It was anticipated that the use of **4** would hinder the formation of cyclic species and also lessen the possibility of oxidation of the hydroquinone structure to a benzoquinoid structure.

Reaction of 3,5-difluorobenzophenone, **2**, with a slight excess of 4-methoxyphenol under typical NAS conditions (NMP, K<sub>2</sub>CO<sub>3</sub>, heat) provided the corresponding protected bisphenol in good yield. Deprotection of the phenolic groups was achieved via reaction with HBr in acetic acid to afford the desired bisphenol, 3,5-bis(4-hydroxyphenoxy)benzophenone, **4**, in good yield. The structure of **4** was confirmed via GC/MS analysis as well as <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

The synthesis of *m*-PEEK was then carried out as depicted in Scheme 2. Reaction of equimolar amounts of **2** and **4**, at 185 °C for 48 h, resulted in the formation of *m*-PEEK, **5**, with a weight average molecular weight, *M*<sub>w</sub>, of 15,600 Daltons (Da). Structural characterization was provided via a combination of <sup>1</sup>H and <sup>13</sup>C NMR (Fig. 2a) spectroscopy, which both showed the presence of all of the anticipated peaks. As expected, *m*-PEEK was soluble in a variety of solvents ranging from tetrahydrofuran (THF) and chloroform to *N,N*-dimethylacetamide (DMAc). Differential scanning calorimetry (DSC) indicated that *m*-PEEK was completely amorphous, with only a glass transition temperature, *T*<sub>g</sub>, of 105 °C observed in heating



**Scheme 2.** Synthesis of *m*-PEEK, **5**, and P<sub>50</sub>-alt-*m*-P<sub>50</sub> Copolymer, **6**.

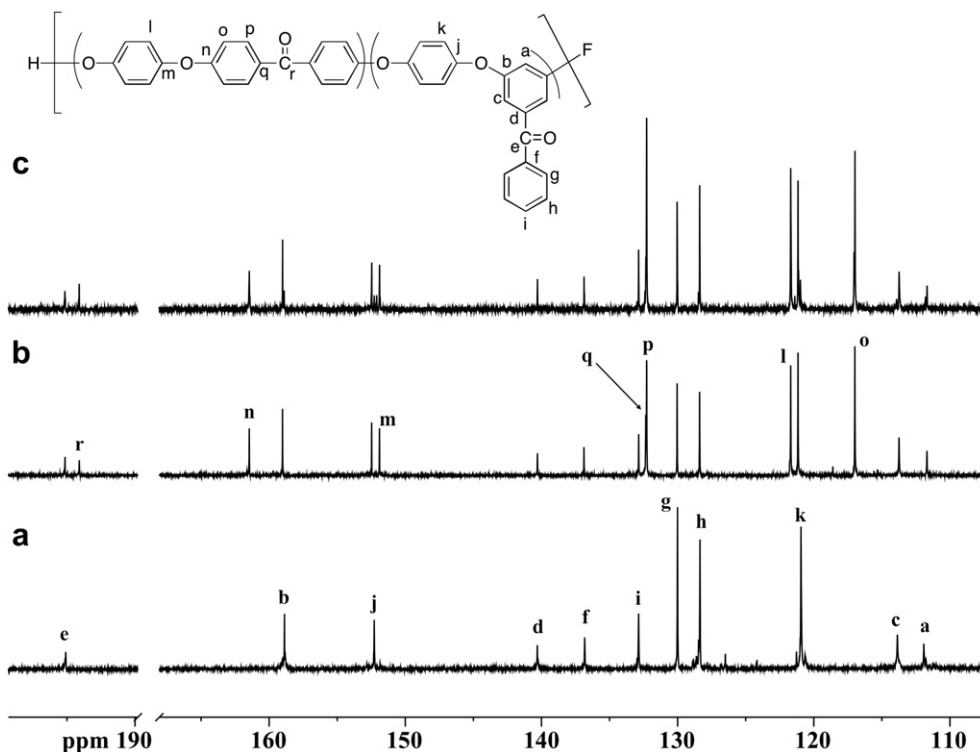


Fig. 2. 75.5 MHz  $^{13}\text{C}$  NMR spectra ( $\text{CDCl}_3$ ) of (a) *m*-PEEK (**5**), (b) copolymer **6**, and (c) copolymer **7a**.

ramps up to 400 °C (see Fig. 3). The somewhat low  $T_g$  value, compared to PEEK (144 °C), is most likely a result of the highly flexible poly(phenylene oxide), PPO, backbone (Fig. 1,  $T_g$  of 95 °C) and the lack of any crystalline regions. The thermal stability of *m*-PEEK was evaluated via thermogravimetric analysis (TGA) and it was found that the 5% weight loss temperature ( $T_{d-5\%}$ ) was 428 °C, somewhat less thermally stable than PEEK. However, this might also be attributed to the lack of any crystallinity in *m*-PEEK.

To explore the impact of incorporating *m*-PEEK segments into PEEK, an alternating copolymer, **6**, was prepared by reacting equal amounts of **1** with **4** at 185 °C for 15 h. The resulting polymer was soluble in chloroform, THF, and NMP, which allowed the polymer to be fully characterized (see Table 1). The  $M_w$  was determined to be 62,500 Da with a polydispersity index of 4.8. The  $^{13}\text{C}$  NMR spectrum

(Fig. 2b) confirmed the presence of all of the expected signals from both the PEEK and *m*-PEEK components. Thermal analysis of this sample also indicated a completely amorphous material with only a  $T_g$ , 127 °C, being observed in heating ramps up to 400 °C (Fig. 3).

In an effort to enhance the potential for crystallization, a series of copolymers, in which progressively decreasing levels of *m*-PEEK segments were introduced, was prepared as outlined in Scheme 3. For discussion purposes the copolymers will be labeled  $P_{xx}\text{-co-}m\text{-}P_{xx}$  where  $xx$  is the mol% of each type of repeat unit while P and *m*-P represent PEEK and *m*-PEEK, respectively. The synthesis of a more PEEK-like structure required the synthesis of an alternative bisphenol, 4,4'-bis-(4-hydroxyphenoxy)benzophenone, **3**, which was prepared according to the procedure reported by Hwang et al. [23] As shown in Scheme 3, reaction of equimolar amounts of **2** with **3**, to form **7a**, provided the same alternating ( $P_{50}\text{-alt-}m\text{-}P_{50}$ ) material prepared via the pendant bisphenol route (**1** + **4**, Scheme 2), **6**, which was confirmed by NMR spectroscopy (Fig. 2c). Because it contains one “built in” PEEK repeat unit, in addition to the requisite hydroquinone, this alternative bisphenol afforded the opportunity to prepare more “PEEK-like” copolymers.

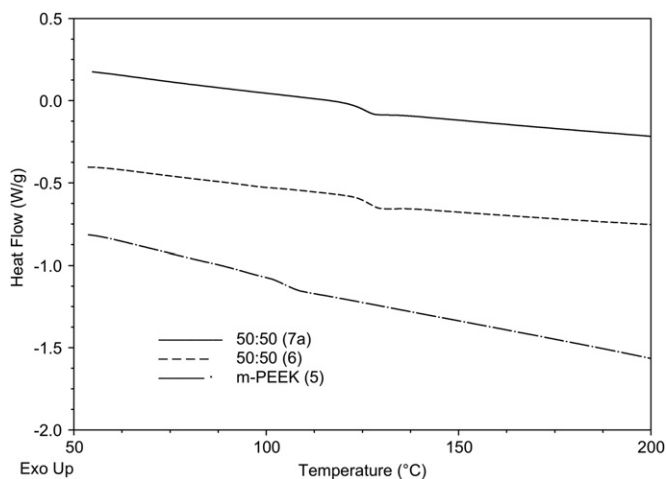


Fig. 3. DSC traces (2nd heat) of *m*-PEEK, **5**, and the alternating copolymers **6** and **7a**.

Table 1

Formulations and molecular weight data for polymers **5**, **6**, and **7a–e**. All reactions were performed in NMP at a temperature of 185 °C.

Polymer	Bisphenol	<b>1</b>	<b>2</b>	Molar ratio	1st step (h)	2nd step (h)	% Yield	$M_w$ (Da)	PDI
<b>5</b>	<b>4</b>	0	1	0:100	48	—	42%	15,600	3.1
<b>6</b>	<b>4</b>	1	0	50:50	15	—	45%	62,500	4.8
<b>7a</b>	<b>3</b>	0	1	50:50	24	—	62%	45,600	2.6
<b>7b</b>	<b>3</b>	0.5	0.5	75:25	16	8	71%	—	—
<b>7c</b>	<b>3</b>	0.6	0.4	80:20	16	8	75%	—	—
<b>7d</b>	<b>3</b>	0.7	0.3	85:15	16	8	49%	—	—
<b>7e</b>	<b>3</b>	0.8	0.2	90:10	16	8	77%	—	—

Solubility characteristics of polymers **5**, **6**, and **7a–e**. Solubility tests were performed with 3 mg samples in 1 mL of the solvent.

Solvent	<b>5</b>	<b>6</b>	<b>7a</b>	<b>7b</b>	<b>7c</b>	<b>7d</b>	<b>7e</b>
CHCl <sub>3</sub>	+	+	+	—	—	—	—
THF	+	+	+	—	—	—	—
DMF	+	+	+	—	—	—	—
DMSO	+	+	+	+/-	—	—	—
DMAC	+	+	+	+	—	—	—
NMP	+	+	+	+	+/-	+/-	—
Toluene	—	—	—	—	—	—	—

— = insoluble.

The solubility characteristics of the series are summarized in Table 2 and it is readily apparent that the more PEEK-like structures possessed considerably lower solubility in all of the solvents tested. While the P<sub>50</sub>-alt-*m*-P<sub>50</sub> sample was soluble in THF, chloroform, etc., the P<sub>75</sub>-co-*m*-P<sub>25</sub>, was insoluble in THF and chloroform,

however, it was soluble in room temperature DMAc, and NMP, but required heating in DMSO. As expected, the higher percentages of PEEK segments lead to diminished solubility properties. For example, the P<sub>85</sub>-co-*m*-P<sub>15</sub> sample was only soluble in hot NMP while the P<sub>90</sub>-co-*m*-P<sub>10</sub> was insoluble, even in hot NMP. Unfortunately, the limited solubility prevented the determination of  $M_w$  values for all of the samples with PEEK contents above 50%.

### 3.2. Thermal properties

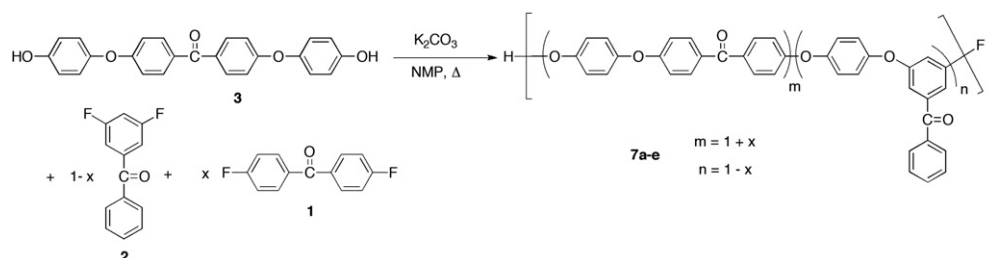
The DSC cooling curves and the second heating traces for **7a–e** are shown in Fig. 4a and b, respectively. In the cooling curves all of the polymers displayed a glass transition temperature,  $T_g$ , however, two of the samples, **7d** and **7e**, also displayed a crystallization temperature,  $T_c$ , indicating that they were semi-crystalline materials. Since these two samples had 85 and 90% of PEEK segments, the observation of crystallization was not unexpected. The observed  $T_g$  values showed a significant increase as the ratio of PEEK to *m*-PEEK was increased. For example, the  $T_g$  of P<sub>50</sub>-alt-*m*-P<sub>50</sub> (**7a**) was 128 °C, while that of P<sub>85</sub>-co-*m*-P<sub>15</sub> (**7d**) increased to 148 °C. The increased values of  $T_g$  at higher levels of PEEK can be attributed to both the change in backbone structure and the presence of some crystallinity.

The  $T_g$ 's observed for **7a–e**, in the second heating traces, essentially mirrored those from the cooling curves, however, the transition was less intense at higher ratios of PEEK to *m*-PEEK. The

Thermal analysis data for polymers **5**, **6**, and **7a–e**.

Polymer	TGA <sup>a</sup>		DSC cooling curve <sup>b</sup>			DSC 2nd heating curve <sup>c</sup>				
	N <sub>2</sub> T <sub>d</sub> -5% (°C)	Air T <sub>d</sub> -5% (°C)	T <sub>g</sub> (°C)	T <sub>c</sub> (°C)	ΔH (J/g)	T <sub>g</sub> (°C)	T <sub>c</sub> (°C)	ΔH (J/g)	T <sub>m</sub> (°C)	ΔH (J/g)
<b>5</b>	428	426	104	—	—	105	—	—	—	—
<b>6</b>	530	519	124	—	—	127	—	—	—	—
<b>7a</b>	480	467	128	—	—	126	—	—	—	—
<b>7b</b>	508	476	136	—	—	137	—	—	—	—
<b>7c</b>	519	511	140	—	—	138	216	8.6	284	10.3
<b>7d</b>	529	517	148	226	25.9	143	—	—	307	19.1
<b>7e</b>	531	522	154	254	33.4	147	—	—	316	27.2

<sup>c</sup> Heating rate of 10 °C/min.



**Scheme 3.** Synthesis of P<sub>m</sub>-co-meta-P<sub>n</sub> Copolymers, **7a–e**.



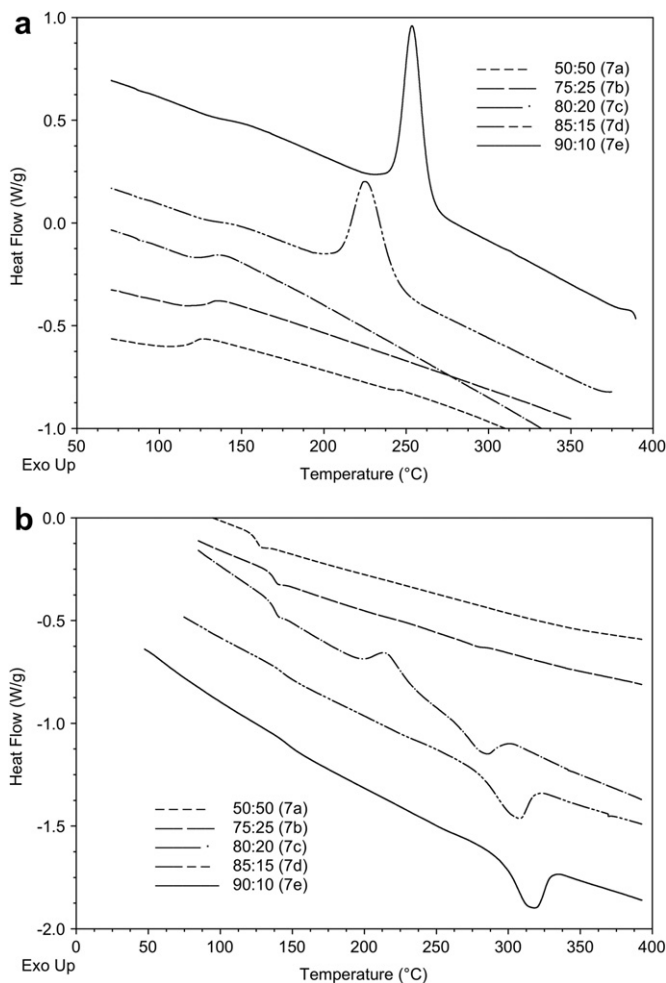


Fig. 4. DSC traces of copolymers **7a–e** under nitrogen: (a) first cooling curves and (b) second heating curves.

P<sub>80</sub>-co-*m*-P<sub>20</sub> (**7c**) sample displayed both a  $T_c$  (216 °C) and melting temperature,  $T_m$ , (284 °C) indicating that it possessed the ability to crystallize. Both the P<sub>85</sub>-co-*m*-P<sub>15</sub> (**7d**) and P<sub>90</sub>-co-*m*-P<sub>10</sub> (**7e**) samples displayed very weak  $T_g$ 's, but quite visible  $T_m$ 's. The enthalpy for the  $T_m$  increased substantially on going from **7c** to **7d** to **7e** (10.3, 19.1, and 27.2 J/g) and the  $T_m$  also shifted to higher values, 284, 307, and 316 °C, respectively. While the observed  $T_m$  values are significantly lower than that of PEEK itself, which has a  $T_m$  of 343 °C, the materials, with the exception of **7e**, also displayed significantly better solubility characteristics.

### 3.3. Crystallinity via X-ray diffraction

Confirmation of the semi-crystallinity present in **7c–e** was provided through powder X-ray diffraction studies as depicted in Fig. 5. Polymer **7e** exhibited the most noticeable diffractions, located at ~19, 21, 23, and 29°, which are quite similar to the (110), (111), (200), and (211) reflections that are the reported values for PEEK [17,24]. As the percentage of PEEK segments decreased, the distinct signals broadened and eventually disappeared into the amorphous halo (samples **6** and **7a**), which is consistent with the observations from the DSC analysis. Interestingly, the diffraction pattern for **7b** seems to indicate the presence of a very low level of crystallinity, which was not readily observed in the corresponding DSC traces.

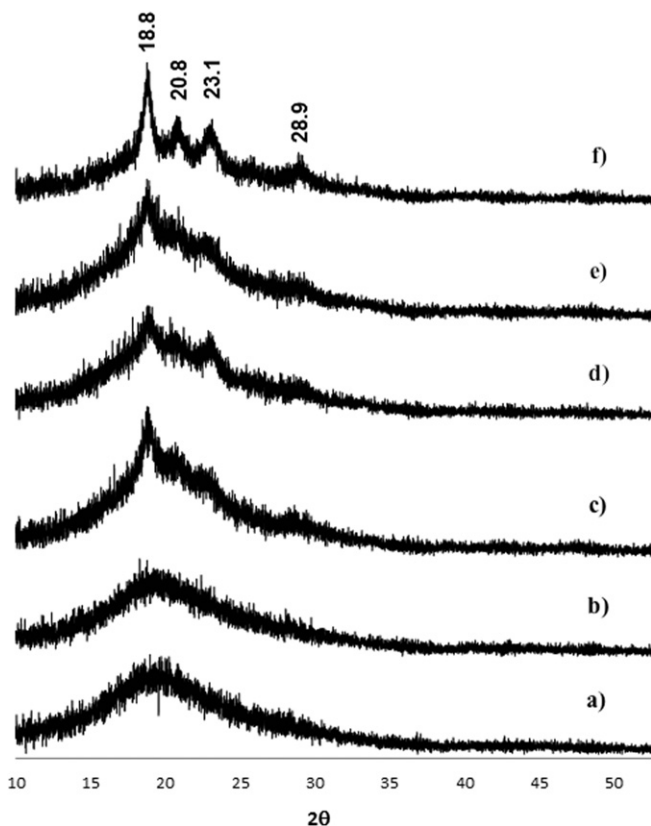


Fig. 5. X-ray diffraction patterns of (a) polymer **6**, (b) **7a**, (c) **7b**, (d) **7c**, (e) **7d**, and (f) **7e**.

### 4. Conclusions

PEEK analogs (*m*-PEEK), based on 3,5-difluorobenzophenone, **2**, were prepared by polycondensation reactions with two oligomeric bisphenols, 4,4'-bis(4-hydroxyphenoxy)benzophenone, **3**, and 3,5-bis(4-hydroxyphenoxy)benzophenone, **4**. In both cases, completely amorphous polymers resulted, even with the “built in” PEEK segments found in **3**. The glass transition temperatures of these two polymers were 127 and 105 °C, respectively. Semi-crystalline PEEK analogs were prepared using **3** and varying ratios of 4,4'-difluorobenzophenone, **1**, and **2**. The samples with 80 mol% or higher of PEEK segments possessed some degree of crystallinity, as determined by DSC and X-ray diffraction, but were also soluble, to a limited extent in organic solvents such as NMP. The glass transition temperatures,  $T_g$ , of the copolymers increased from 126 to 147 °C as the percentage of PEEK was increased from 50 to 90 mol%. The melting temperatures,  $T_m$ , also showed a similar trend with the 80:20 and 90:10 samples displaying  $T_m$  values of 284 and 316 °C, respectively. In addition, the use of monomer **2** affords PEEK systems that carry pendant benzoyl groups, which provide versatile sites for the introduction of functional groups and exploration of this particular aspect is ongoing.

### Acknowledgments

This material is based upon work supported by the National Science Foundation under CHE-1012392. Professor David Grossie of Wright State University is acknowledged for his assistance in obtaining the X-ray diffraction data.

## References

- [1] Hergenrother PM. High Perf Polym 2003;15:3–45.
- [2] McGrail PT. Polym Int 1996;41(2):103–21.
- [3] Rose JB, Staniland PA. vol. 4, 320,224. US, 1982.
- [4] Teasley MF, Hsiao BS. Macromolecules 1996;29(20):6432–41.
- [5] Staniland PA. Poly(ether ketone)s. In: Allen G, Bevington JC, editors. Comprehensive polymer science, vol. 5. Oxford: Pergamon; 1989. p. 483–97.
- [6] Parthiban A, Guen AL, Yansheng Y, Hoffmann U, Klapper M, Mullen K. Macromolecules 1997;30:2238–43.
- [7] Koch T, Ritter H. Macromolecules 1995;28:4806–9.
- [8] Wang F, Roovers J. Macromolecules 1993;26:5295–302.
- [9] Xing P, Robertson GP, Guiver MD, Mikhailenko SD, Wang K, Kaliaguine S. J Membr Sci 2004;229:95–106.
- [10] Risse W, Sogah DY. Macromolecules 1990;23:4029–33.
- [11] Cheng L, Ying L, Feng J, Wang CY, Li JL, Xu Z. J Polym Sci Part A Polym Chem 2007;45(8):1525–35.
- [12] Wu T, Liu P, Shi M, Lu J, Ye G, Xu J. Polym Int 2011;60:1318–23.
- [13] Carlier V, Devaux J, Legras R, Bunn A, McGrail PT. Polymer 1994;35(2):415–22.
- [14] Ben-Haida A, Colquhoun HM, Hodge P, Williams DJ. Macromolecules 2006;39:6467–72.
- [15] Kricheldorf HR, Vakhtangishvili L, Schwartz G, Prosenc M. J Polym Sci Part A Polym Chem 2005;43:6233–46.
- [16] Blundell DJ. Polymer 1992;33:3773–6.
- [17] Gardner KH, Hsiao BS, Matheson Jr RR, Wood BA. Polymer 1992;33:2483–95.
- [18] Shibata M, Yosomiya R. Macromol Rapid Commun 1997;18:99–105.
- [19] Attwood TE, Dawson PC, Freeman JL, Hoy RJ, Rose JB, Staniland PA. Polymer 1981;22:1096.
- [20] Kaiti S, Himmelberg P, Williams J, Abdellatif M, Fossum E. Macromolecules 2006;39:7909–14.
- [21] van Beek D, Fossum E. Macromolecules 2009;42:4016–22.
- [22] Tienda K, Yu Z, Constandinidis F, Fortney A, Feld WA, Fossum E. J Polym Sci Part A Polym Chem 2011;49:2908–15.
- [23] Hwang S-H, Lee G-S, Lee K-K, Jung J-C. Polym Adv Technol 2001;12:441–4.
- [24] Gardner KH, Hsiao BS, Faron KL. Polymer 1994;35:2290–5.