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New Poly(aryl ether ketone) Copolymers Containing 1,5-Napthalene Rings

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A new monomer 1,5-bis(4-(4′-fluorobenzoyl) phenoxy) naphthalene(1,5-BFPN) was synthesized with 4,4′-difluorobenzophenone(DFB) and 1,5-dihydroxynaphthalene(DHN), and the new monomer was characterized by X-Ray single crystal diffraction. The polycondensation of 1,5-BFPN with PEEK oligomer in diphenyl sulfone (DPS) in the presence of an excess of sodium carbonate and potassium carbonate as a condensation reagent was carried out at 320°C to quantitatively afford the corresponding poly(ether ether ketone-co-ether naphthalene ether ketone) regular copolymers. Thermal analysis of the copolymers showed that the glass transition temperature increased, while the melting temperature decreased with increasing the content of 1,5-BFPN moieties.

Keywords poly(aryl ether ketone), oligomer, single crystal structure

Introduction

Poly(arylene ether ketone)s (PAEKs) are an important class of high performance polymers displaying excellent thermal and chemical stability and good mechanical properties. Since the commercialization of poly(ether ether ketone)(PEEK) by ICI, a number of new PAEKs' have been synthesized in an effort to improve overall properties (1–4).

Meanwhile, it has been reported that poly(aryl ether ketone)s containing naphthalene ring in main chains possess higher T_gs and some of them have better solubility in some organic solvents than PEEK (5–14). By virtue of the possibility of uniformly distributing the phenylene and naphthylene, the copolymers containing different naphthylene molar fractions can be generated in order to improve or modify the inherent characteristics of such polymers. For instance, PEEK is a semi-crystalline polymer, while the PAEKs containing 1,5-naphthylene structure, such as PENEK, is not melt-crystallizable (15). Considering that the naphthylene group maintains the good properties but prevents crystallization, we are interested in investigating the single-crystal studies and diffraction modeling-the first crystallographic characterization crystal behaviors of monomer and characterization of copolymers that contains regular sequences of phenylene and naphthylene, in order to compare their properties with those already reported for PEEK and PENEK (15).

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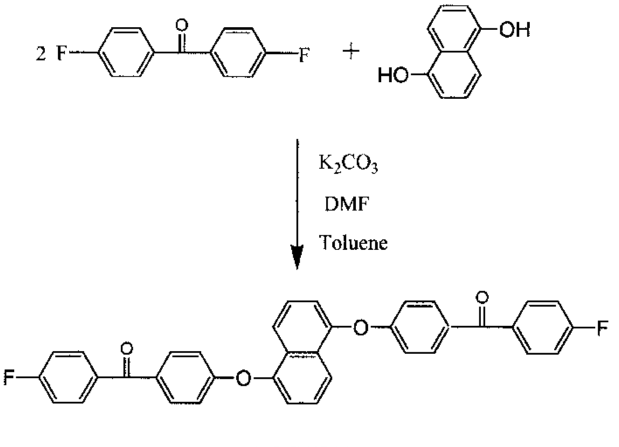
Experimental

Materials

4,4′-Difluorobenzophenone (DFB, purity 98%, industrial grade) and hydroquinone (HQ, purity 98%, industrial grade), supplied by Yanji Chemical Plant, China, were dried in vacuum at 70°C for 6 h before polymerization. Diphenyl sulfone (DPS, purity 98%, industrial grade, supplied by Yanji Chemical Plant in China) was recrystallized in acetone and then dried in vacuum oven at 70°C for 8 h. 1,5-Dihydroxynaphthalene (1,5-DHN, analysis reagent) purchased from ACROS ORGANICS in Belgium was dried at 70°C in a vacuum oven. All the monomers and other reagents were used without further purification.

Synthesis of Monomer 1,5-bis(4-(4′-fluorobenzoyl) phenoxy) naphthalene(1,5-BFPN)

A 250 mL four-neck round bottom flask equipped with nitrogen inlet, thermometer, overhead stirrer, and condenser was charged with DFB (43.6 g, 0.2 mol), potassium carbonate (5.53 g, 0.04 mol), toluene (10 mL) and DMF (100 mL). The reaction mixture was purged with nitrogen for 10 min and then heated with stirring at about 120°C for about 1 h. 1,5-DHN (3.2 g, 0.02 mol) was dissolved into 20 mL DMF, and then the solution was dropped into the flask in 1 h. The reaction temperature was maintained at 120°C for 3 h to remove the produced water by azeotropic distillation with toluene and then raised up to 165°C for about 4 h. The mixture was poured into 500 mL of water and the solid was washed with ethanol several times, greenish yellow powder was obtained.

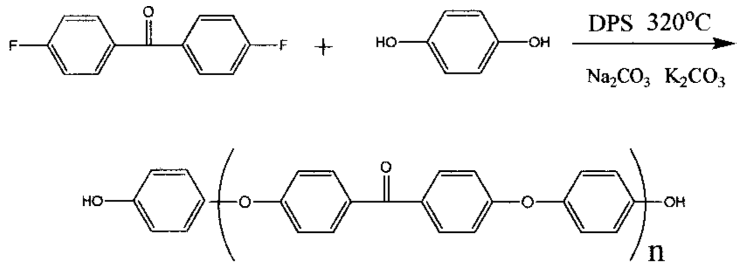


1,5-BFPN

(Yield: 80%. m.p. 216–217°C(DSC). m/z = 556. Elem. Anal. $C_{36}H_{22}F_2O_4$: Calcd.: C 77.69, H 3.98; Found: C 77.47, H 3.73. IR(KBr, cm^{-1}): 2924, 1643, 1597, 1398, 1247, 1225, 1155, 930, 862, 779 and 677. ^{1}H NMR (CDCl$_3$, δ, ppm): $\delta = 7.91$ (d, 2H), 7.83 (dd, 4H), 7.81 (dd, 4H), 7.62 (s, 2H), 7.40 (s, 4H), 7.35 (d, 2H), 7.18 (d, 4H). ^{13}C NMR (CDCl$_3$, δ, ppm) $\delta = 193.02$, 165.42, 161.25, 150.45, 133.80, 132.29, 131.59, 127.98, 126.99, 118.21, 116.96, 116.74, 115.60, 115.42).

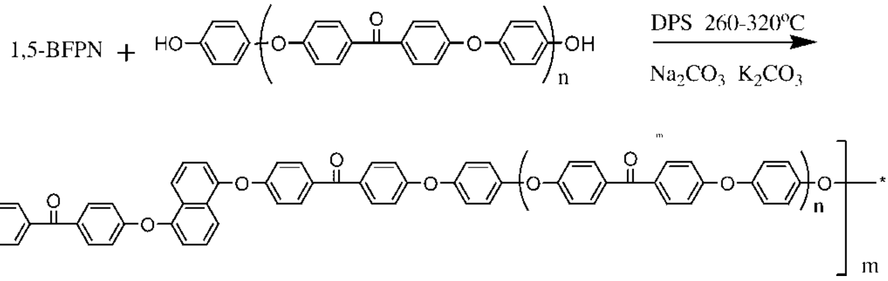
Synthesis of PEEK Oligomer

Dihydroxy-terminated PEEK oligomer was prepared by the reaction of HQ and DFB in the presence of sodium carbonate and potassium carbonate as a condensation reagent at 320°C as depicted below:



Synthesis of Poly(ether ether ketone-co-ether naphthalene ether ketone) Copolymers

P(EEK-co-ENEK) regular copolymers were prepared from the 1,5-BFPN and oligomer via a nucleophilic aromatic substitution reaction. A typical reaction condition for the copolymer synthesis is as follows: PEEK oligomer was prepared first, but was not isolated from the reaction mixture. 1,5-BFPN, which had been isolated and characterized, was added to the melting mixture, the reaction mixture was maintained at 260–320°C for 3–6 h. The copolymers were precipitated by pouring the hot reaction mixture into a large amount of distilled water, filtered, and washed with acetone and distilled water several times. Drying at 120°C for 12 h produced greenish yellow copolymers.



Measurements

Inherent viscosities of the copolymers were measured at 25°C on a 0.1 g/dL solution in 98% sulfuric acid (16).

Infrared spectral analysis was performed on a Nicolet Impact 410 FTIR. ^{1}H (500 MHz) and ^{13}C (125 MHz) spectra were recorded in DMSO-d solutions on a Bruker 510 MHz NMR, and the result was reported in ppm from tetramethylsilane in the δ scale. X-Ray diffraction of a single crystal was carried out with a Siemens P_4 diffractometer (Mo Kα radiation, $\lambda = 0.71073$Å) using ω-scans. Computation relating to the single-crystal structure was carried out using the SHELXTL-97 program system. Glass transition temperatures (T_g) were determined using Mettler Toledo DSC 821e differential scanning calorimetry (DSC). The heating rate was 20°C/min. In all experiments, the original samples were heated from 80°C to 400°C. The values of the glass transition temperature T_g were taken as the temperature of the midpoint of the increment of the specific heat capacity. Thermal gravimetric analyses (TGA) were determined in air using a heating rate of 20°C/min and copolymers were contained within open aluminum pans on a Perkin Elmer TGA-7. Wide-angle X-ray diffraction patterns were recorded in the reflection mode at room temperature by using a Rigaku D/max-rA. Graphite monochromator and CuK_α radiation were used.

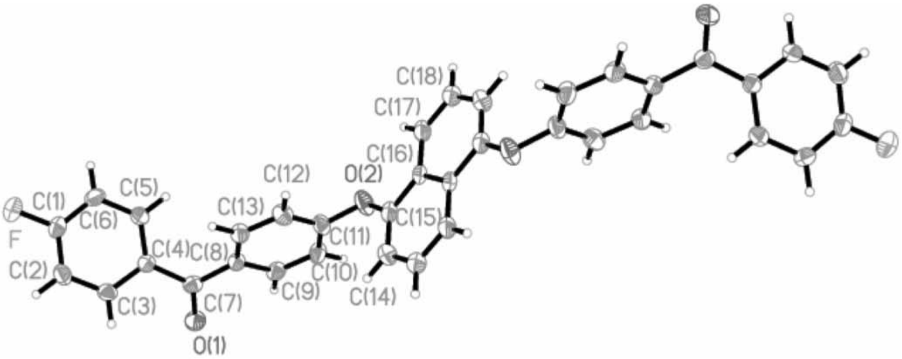


Figure 1. Molecular structure of 1,5-bis(4-(4′-fluorobenzoyl) phenoxy) naphthalene(1,5-BFPN). The hydrogen atoms are omitted for clarity.

Results and Discussion

1,5-bis(4-(4′-fluorobenzoyl) phenoxy) naphthalene(1,5-BFPN) was synthesized via aromatic nucleophilic substitution reaction between the 4,4′-Difluorobenzophenone (DFB) and 1,5-dihydroxynaphthalene (1,5-DHN) in potassium carbonate as a condensation reagent with a high yield (80%). The structure of the monomer was confirmed by mass spectrometry, IR, NMR spectroscopy, and elemental analysis.

Table 1
Atomic coordinates of the 1,5-BFPN

Name	x	y	z
F	0.265	0.078	0.322
O1	0.867	0.253	0.320
O2	0.251	0.430	0.287
C1	0.361	0.122	0.323
C2	0.563	0.125	0.401
C3	0.659	0.169	0.402
C4	0.549	0.208	0.326
C5	0.344	0.202	0.251
C6	0.246	0.158	0.248
C7	0.663	0.253	0.320
C8	0.549	0.299	0.316
C9	0.656	0.337	0.236
C10	0.557	0.381	0.229
C11	0.356	0.386	0.310
C12	0.246	0.349	0.395
C13	0.346	0.306	0.395
C14	0.334	0.454	0.588
C15	0.208	0.456	0.441
C16	0.026	0.486	0.425
C17	−0.104	0.488	0.266
C18	−0.282	0.517	0.261

To provide a starting point for the structure analysis of polymer, a single crystal molecular structure determination on the model compound (1,5-BFPN) has been carried out. Drawing for the molecular structures is in Figure 1. The structure of 1,5-BFPN revealed a monoclinic unit cell, space group $P2_1/c$. Although the molecule has potential for crystallographic inversion symmetry, this is not in fact adopted. 1,5-BFPN shows a fully extended chain conformation (Figure 1) with bridge-bond angles averaging 121.7° at the carbonyl groups and 117.7° at the ether linkages. Atomic coordinates for 1,5-BFPN are given in Table 1, and bond lengths and bond angles for the asymmetric unit are shown in Table 2. (Crystal data: $C_{36}H_{22}F_2O_4$, $M = 556.54$, Monoclinic, space group $P21/n$, $a = 6.167(3)$Å, $b = 28.570(11)$Å, $c = 7.456(2)$Å, $U = 1313.7(9)$Å^3, $Y = 293$K, $D_C = 1.407\,\mathrm{g/cm^3}$, $F(000) = 576$)

Figure 2 shows the DSC traces of the quenched samples of the copolymers on the heating run. The values of T_g and T_m for the copolymers are shown in Table 3. The T_g increased with increasing the content of naphthalene moieties. For the copolymers with

Table 2

Bond lengths [Å] and bond angles [°] for the 1,5-BFPN

F-C(1)	1.357	C(8)-C(9)	1.392
O(1)-C(7)	1.234	C(9)-C(10)	1.375
O(2)-C(15)	1.391	C(10)-C(11)	1.379
O(2)-C(11)	1.399	C(11)-C(12)	1.387
C(1)-C(6)	1.366	C(12)-C(13)	1.381
C(1)-C(2)	1.377	C(14)-C(15)	1.348
C(2)-C(3)	1.373	C(14)-C(18)#1	1.398
C(3)-C(4)	1.395	C(15)-C(16)	1.423
C(4)-C(5)	1.390	C(16)-C(16)#1	1.420
C(4)-C(7)	1.486	C(16)-C(17)	1.414
C(5)-C(6)	1.392	C(17)-C(18)	1.364
C(7)-C(8)	1.494	C(18)-C(14)#1	1.398
C(8)-C(13)	1.390		
C(15)-O(2)-C(11)	117.7	C(10)-C(9)-C(8)	120.9
C(6)-C(1)-C(2)	123.1	C(11)-C(10)-C(9)	119.3
C(6)-C(1)-F	118.5	C(10)-C(11)-O(2)	117.6
C(2)-C(1)-F	118.4	C(10)-C(11)-C(12)	121.3
C(1)-C(2)-C(3)	118.3	O(2)-C(11)-C(12)	120.8
C(2)-C(3)-C(4)	121.2	C(13)-C(12)-C(11)	118.6
C(5)-C(4)-C(3)	118.4	C(12)-C(13)-C(8)	121.1
C(5)-C(4)-C(7)	123.3	C(15)-C(14)-C(18)#1	120.2
C(3)-C(4)-C(7)	118.2	C(14)-C(15)-O(2)	123.6
C(4)-C(5)-C(6)	121.2	C(14)-C(15)-C(16)	121.6
C(1)-C(6)-C(5)	117.8	O(2)-C(15)-C(16)	114.8
O(1)-C(7)-C(4)	119.2	C(15)-C(16)-C(16)#1	117.6
O(1)-C(7)-C(8)	119.2	C(15)-C(16)-C(17)	122.8
C(4)-C(7)-C(8)	121.7	C(16)#1-C(16)-C(17)	119.6
C(13)-C(8)-C(9)	118.7	C(18)-C(17)-C(16)	120.0
C(13)-C(8)-C(7)	123.4	C(17)-C(18)-C(14)#1	121.0
C(9)-C(8)-C(7)	117.7		

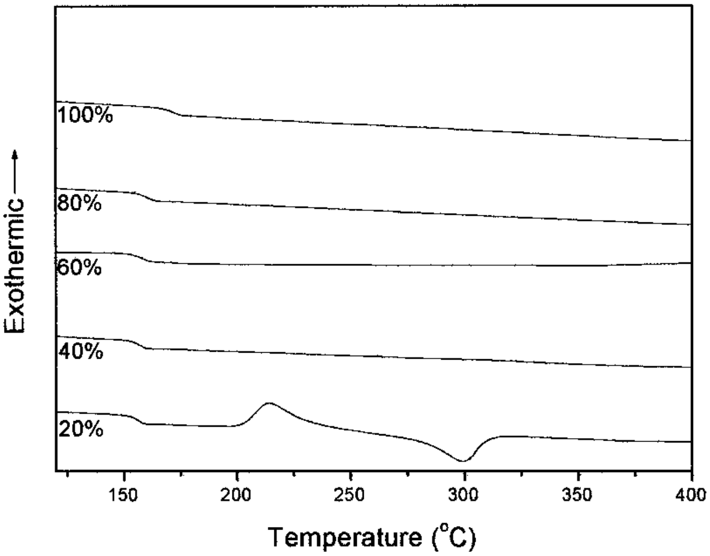


Figure 2. DSC traces of PAEK copolymers containing 1,5-naphthalene moieties with the different molar fractions of 1,5-BFPN.

a 1,5-BFPN molar fraction of 0.20, the T_m decreased and T_c showed the reverse tendency compared with PEEK (1). When the molar fraction of 1,5-BFPN is over 0.4, the clear cold-crystallization temperature (T_c) and T_m cannot be detected. These results are assumed to be attributed to the disturbance of the segmental movement and the destruction of the symmetry and regularity of the molecular chains due to the introduction of the naphthalene moiety. The 5.0% wt loss temperatures (T_d) of the copolymers, which are similar to PEEK, are shown in Table 3 (15).

The results of WAXD measurement of the copolymers are shown in Figure 3. The pattern of diffraction peaks, the value of 2θ for each diffraction peak is the same as PEEK, suggesting that the crystal structure of the copolymer is a rhombic system in the

Table 3
Properties of poly (aryl ether ketone)s copolymers containing 1,5-naphthalene moieties

No.	DFB (mol)	Oig1 (mol)	Molar fraction of 1,5-BFPN[a]	Molar fraction of DHN[b]	η_{inh}[c] (dL/g)	T_g (°C)	T_m (°C)	T_d[d] (°C)
1	0.08	0.02	0.2	0.17	0.81	155	299	544
2	0.06	0.04	0.4	0.29	0.73	156	—	552
3	0.04	0.06	0.6	0.38	0.72	157	—	564
4	0.02	0.08	0.8	0.44	0.70	159	—	563
5	0	0.10	1.0	0.50	0.68	170	—	545

[a] Molar ratio of 1,5-BFPN/(1,5-BFPN +DFB).
[b] Molar ratio of 1,5-DHN/(1,5-DHN + HQ).
[c] Measured at the concentration of 0.1 g/dL.
[d] T_d is the temperature at which the weight loss of the polymer is 5.0%.

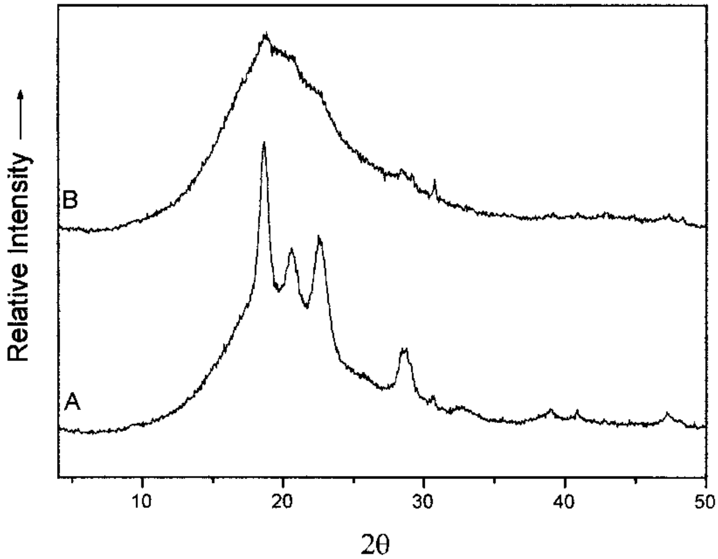


Figure 3. WAXD patterns of the copolymers with the molar fraction of 1,5-BFPN. (A) 0.20, (B) 0.40.

same manner as PEEK (17, 18). The intensity of diffraction peaks decreased with increasing content of naphthalene moieties. As the molar fraction of 1,5-BFPN is over 0.4, the copolymers became amorphous. It can therefore, be presumed that the segments containing naphthalene moieties in the copolymer are not in the crystal unit cell of the copolymer but in the amorphous phase between the crystalline lamellae.

Conclusions

A new monomer namely 1,5-bis(4-(4′-fluorobenzoyl) phenoxy) naphthalene(1,5-BFPN), was synthesized by nucleophilic reaction and its structure was characterized by X-Ray single crystal diffraction. A series of poly(aryl ether ketone) regular copolymers containing 1,5-naphthalene moieties was synthesized by the PEEK oligomer and 1,5-BFPN reaction. The thermal behavior and crystallization ability of such copolymers depend on molar ratio. The T_g increases with the increasing molar fraction of 1,5-BFPN.

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