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Synthesis and Characterization of Poly(ether ether ketone)s with (2,5-dihydroxy)phenyl Side Group

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A new monomer, (2,5-dimethoxy)phenylhydroquinone (DMPH), was prepared in a two-step synthetic procedure. One aromatic poly(ether ether ketone)s with 2,5-dimethoxy phenyl side group (DMP-PEEK) was synthesized via an aromatic nucleophilic substitution reaction with 4,4'-difluorobenzophenone (DFB). Poly(ether ether ketone)s with 2,5-dihydroxy phenyl side group (DHP-PEEK) was obtained via hydrolysis of methoxy group on the DMP-PEEK. Both of the high molecular weight polymers could be obtained despite the steric effect of the bulky pendant groups. The two polymers have good solubility at room temperature.

Keywords: aromatic poly(ether ether ketone)s; hydroxyl; adhesion property; functional polymers

1 Introduction

Poly(ether ether ketone) (PEEK) is a high-performance thermoplastic exhibiting excellent mechanical properties, thermal stability and environmental resistance, which had been widely used for constructive elements in industry (1–6). Recently, this polymer has been found new developments in the medical sector and biotechnology. Moreover, carbon-fiber-reinforced PEEK gave rise to composites exhibiting excellent biomechanical compatibility with bone tissues (7).

However, the native PEEKs have been shown to be a poor substrate (8), extremely reluctant to allow cellular adhesion. Therefore, the modification would be easily detected (9–13). The preparation of substrate for cell cultivation, from the surface-modified PEEK film, has been reported (14–16). The surface-modified PEEK film displays a high density of hydroxyl functions, in order to (a) increase the hydrophilicity of the substrate surface and its capacity for adsorbing/desorbing proteins (17) and, (b) introduce reactive anchorage points (the hydroxyl functions) for the covalent coupling of biologically active molecules susceptible to improving biocompatibility by interacting with specific cell receptors

(18). As a result, the presence of surface hydroxyl functions moderately improves the PEEK film cellular adhesion.

In fact, it is difficult for PEEK to be used as thin films because of their poor solubility. In addition, their poor solubility makes the polymerization conditions rigorous. To obtain novel PEEK with a high density of hydroxyl functions and good solubility, we report an efficient method to make the soluble PAEK containing (2,5-dihydroxy) phenyl side group (DHP-PEEK).

2 Experimental

2.1 Materials

4,4-Difluorobenzophenone (mp = 103–104°C) was supplied by Yanji Chemical Plant, China. Tetramethylene sulfone (TMS) was purchased from Jizhou Oil Refinery and purified by distillation under reduced pressure. (2,5-dimethoxy)aniline was provided by Tokyo chemical industry. 1,4-Benzoquinone (Dalian Jizhou Chemical) and other reagent were provided by Aldrich.

2.2 Synthesis of (2,5-dimethoxy)phenylbenzoquinone (DMPB)

Into a 1000 mL beaker equipped with a mechanical stirrer, a dropping funnel, and a thermometer, were placed water (100 mL), ice (100 g) and (2,5-dimethoxy)aniline (76.5 g,

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0.5 mol) and stirred for 5 min. Hydrochloric acid (11.8 M, 169.5 mL) was added dropwise into the stirred mixture through the dropping funnel, and then a concentrated water solution of sodium nitrite (34.5 g, 0.5 mol) was added dropwise. The mixture was stirred at 0–5°C for 2 h and yielded a purple solution.

The resulting solution was filtered and added dropwise to a mixture of 1,4-benzoquinone (54 g, 0.5 mol), sodium bicarbonate (116 g, 3.0 mol) and water (200 mL). The reaction mixture was stirred at 8–12°C for about 2 h and then at room temperature for 2 h. The precipitate was collected by filtration, washed thoroughly with water, and dried at 60°C in a vacuum oven. The product was recrystallized from *n*-butanol (19).

(Yield: 71%. mp: 89°C (DSC). *m/z*: 244. Elem. Anal. Calcd. for C₁₄H₁₂O₄: C, 68.85%; H, 4.95%. Found: C, 68.78%; H, 5.06%. IR (KBr, cm⁻¹): 2967, 2833, 2038, 1657, 1278, 1216, 1053, 1020, 906 and 780. ¹H-NMR (CDCl₃, δ, ppm): 6.95 (dd, *J* = 7.5 Hz, 3.0 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 1H), 6.86 (d, *J* = 4.0 Hz, 1H), 6.80 (s, 1H), 6.73 (d, *J* = 3.0 Hz, 1H), 3.73 (3H), 3.18(3H). ¹³C-NMR (CDCl₃, δ, ppm): 187.68, 185.51, 153.52, 151.35, 145.84, 137.10, 136.11, 134.41, 123.33, 116.18, 116.03, 112.57, 56.33, 55.84.)

2.3 Synthesis of (2,5-dimethoxy)phenylhydroquinone (DMPH)

(2,5-dimethoxy)phenylbenzoquinone (73 g, 0.30 mol), Zn powder (58.9 g, 0.9 mol), and 550 mL of deionized water were placed into a 1000 mL, three-necked flask equipped with a mechanical stirrer, a condenser, and a dropping funnel. The mixture was heated to 90°C with stirring, which was followed by the addition of 72 mL of HCl (11.8 M) dropwise at a rate of a drop every two seconds. After the addition, the reaction mixture was allowed to reflux for 3 h. Then, the hot mixture was filtered. The filtrate was cooled to room temperature and poured into a large amount of deionized water. Thick pink solid was collected and recrystallized from toluene.

Yield: 60%. mp: 160°C (DSC). *m/z*: 200. Elem. Anal. Calcd. for C₁₄H₁₄O₄: C, 68.28%, H, 5.73%. Found: C, 68.22%, H, 5.77%. IR (KBr, V, cm⁻¹): 3382, 2947, 1603, 1511, 1317, 1219, 1047, 812, 631. ¹H-NMR (DMSO, δ, ppm): 6.95 (d, *J* = 9.0 Hz, 1H), 6.84 (dd, *J* = 9.0 Hz, 3.0 Hz, 1H), 6.71 (d, *J* = 3.0 Hz, 1H), 6.67 (d, 8.5 Hz 1H), 6.55 (dd, *J* = 15 Hz, 1H), 6.50 (dd, *J* = 9.0 Hz, 3.0 Hz 1H), 3.70 (3H), 3.64(3H). ¹³C-NMR (DMSO, δ, ppm): 153.2, 151.31, 149.81, 147.53, 129.32, 126.28, 118.10, 117.63, 116.68, 115.21, 113.19, 113.10, 56.49, 55.83).

2.4 Synthesis poly(ether ether ketone)s with (2,5-dimethoxy)phenyl side group (DMP-PEEK)

Polymerization of DMPH with 4,4-Difluorobenzophenone was carried out using the following general procedure. A three-necked flask was equipped with a Dean Stark trap, condenser, mechanical stirrer and nitrogen inlet. To the flask were added

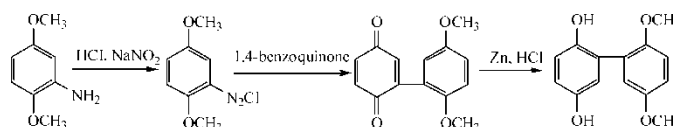
DHPH (3.69 g, 0.015 mol), 4,4'-difluorobenzophenone (3.27 g, 0.015 mol), TMS (20 ml), calculated K₂CO₃ (2.27 g, 0.0165 mol) and toluene (8 ml). The mixture was then heated to reflux for 2 h under nitrogen atmosphere, and then the toluene was distilled from the flask. The mixture was stirred for at 206°C for 5 h. The mixture was poured into 2500 ml of deionized water. After cooling, the polymer was pulverized into powder. The powder was washed by deionized water for several times and dried at 80°C for 24 h at. Finally, DMP-PEEK was obtained as a buff powder.

2.5 Synthesis poly(ether ether ketone)s Containing (2,5-dihydroxy)phenyl Side Group (DHP-PEEK)

To a 250 mL three-necked flask equipped with a magnetic stirrer, a condenser, nitrogen inlet, DMP-PEEK (3 g) and freshly prepared pyridine hydrochloride (100 g) were placed. The mixture was heated under reflux until the solution became homogeneous. It took about 4 h. After being cooled to 120°C, the mixture was poured into water. The polymer was precipitated by pouring the reaction mixture into a blender containing about 250 mL of water, filtered, washed three times with water, and dried to yield 2.6 g (93% yield) as a buff powder.

2.6 Measurements

IR spectra (KBr pellets or films) were measured on a Nicolet Impact 410 Fourier transform infrared (FTIR) spectrometer. ¹H (500 MHz), ¹³C (125.7 MHz) spectra were recorded on a Bruker 510 NMR spectrometer with tetramethyl silane as a reference. Gel permeation chromatograms were obtained on a Waters 410 instrument with tetrahydrofuran (THF) as an eluent at a flow rate of 1.00 mL/min. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC821^e instrument at a heating rate of 20°C/min under nitrogen. The glass-transition temperature (T_g) was taken in DSC curve as the center of the step transition in the second heating run. Thermogravimetric analysis (TGA) was performed on a Netzch Sta 449 thermal analyzer system at a heating rate of 10°C/min in air. The elemental analysis was carried out with a Thermoquest CHNS-O elemental analyzer. Mass spectra were obtained on a Finnigan 4510 mass spectrometer. WAXD was carried out on a Japan D/max-γ A X-ray instrument (Cu Kα radiation).



Sch. 1. Synthesis of the bisphenol monomers.

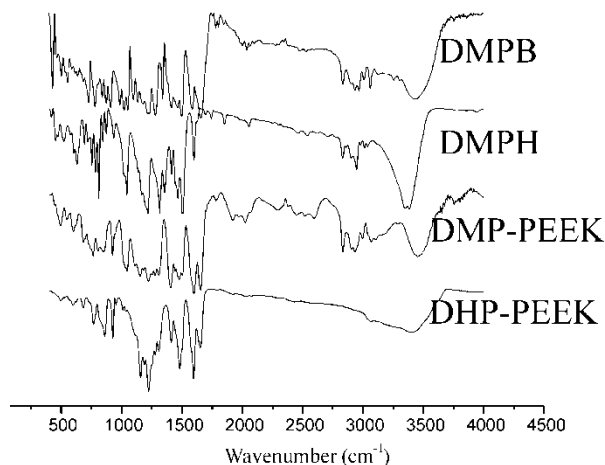


Fig. 1. IR spectrum of DMPB, DMPH, DMP-PEEK and DHP-PEEK.

3 Results and Discussion

3.1 Monomer Synthesis and Characterization

(2,5-Dimethoxy)phenylhydroquinone (DMPH) was synthesized in two steps by the coupling reaction of (2,5-dimethoxy)phenylbenzoquinone with 1,4-benzoquinone in the presence of NaHCO_3 , followed by reduction with Zn/HCl (Scheme 1). The structures of the DMPH and DMPB were confirmed by mass spectrometry, IR, NMR spectroscopy and elemental analysis. In the IR spectra, DMPB shows an absorption band around 1656 cm^{-1} due to symmetric stretching of carbonyl groups. After reduction, this characteristic absorption disappeared, and the characteristic bands of hydroxyl groups around 3382 cm^{-1} appeared (Figure 1). In $^1\text{H-NMR}$ spectra, the chemical shifts and assignments of DMPH are consistent with the expected structure. The peak at 8.32–8.63 ppm of DMPH is assigned to the hydroxyl proton that is absent in the spectrum of DMPB. The peaks at 3.64–3.70 and 6.50–6.96 ppm are assigned to the methoxy and aromatic protons respectively (Figure 2).

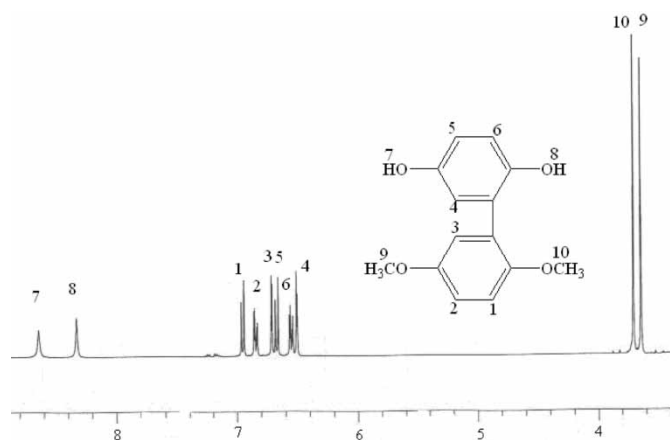
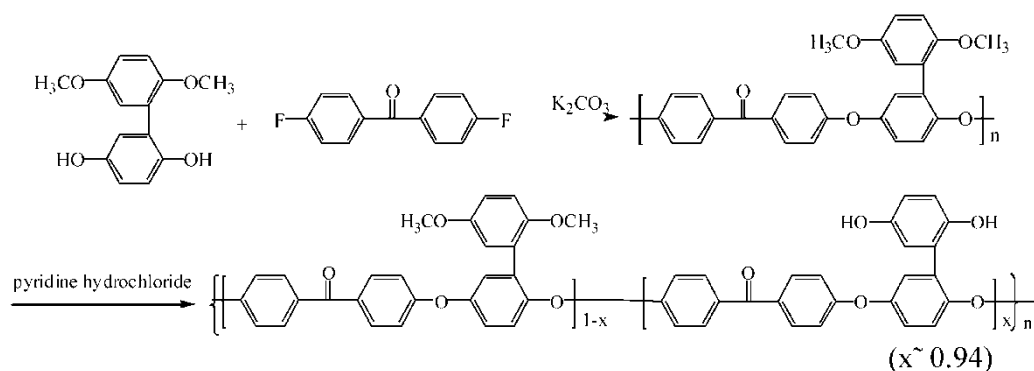


Fig. 2. 500 MHz $^1\text{H-NMR}$ spectrum of DMPH in DMSO-d_6 .

3.2 Polymer Synthesis and Characterization

Polymer with dimethoxyphenyl pendant groups was easily obtained by aromatic nucleophilic polycondensation of DMPH with a stoichiometric amount difluoro monomer. The polymerizations were carried out in the presence of excess potassium carbonate as a base in TMS, as shown in Scheme 2. Toluene was used as an azeotropic agent, and its relative amount determined the bisphenolate forming temperature. Anhydrous potassium carbonate, a weak base, was used to deprotonate the hydroxyl groups. After the completion of bisphenolate formation in 2 h, the reaction temperature was increased to 206°C . Despite the steric hindrance of bulky side groups and the existence of dimethoxy groups would reduce the reactivity of fluorine atoms; dramatically increased viscosity of the reaction systems was observed only about 2.5 h after the completion of bisphenolate formation. Therefore, the high molecular weight polymers were obtained. Gel permeation chromatography (GPC) in THF: Number-average molecular weight (M_n), 30000; index of polydispersity (M_w/M_n), 3.60.

The FTIR spectrum of the polymer supports their structure. All the polymer exhibits the characteristic absorption bands around 1221 cm^{-1} due to aryl ether linkages and around



Sch. 2. Synthesis of DMP-PEEK and DHP-PEEK.

1658 cm^{-1} corresponding to aryl carbonyl groups, characteristic bands of methyl around 2832 cm^{-1} appeared. $^1\text{H-NMR}$ spectra of DMP-PEEK, the assignments of the peaks are in agreement with the proposed structures (Figure 3).

3.3 Synthesis DHP-PEEK

The methyl aryl ether linkage on the polymer backbone is cleavable by acid catalysis. The DMP-PEEK sample powder was placed into pyridine hydrochloride. After heating the mixture system for about 4 h, it indicates conversion from a methoxy group to hydroxyl and that the solubility

of polymer in pyridine hydrochloride dramatically increased. The proportion of conversion was estimated on the basis of $^1\text{H-NMR}$ spectrum (Figure 4). The ratio of integrated areas of the peaks corresponding to the protons in residual methoxy and in ortho-position of carbonyl indicated that the proportion of conversion is 94%. The FTIR spectrum of the polymer, as well, showed the result of demethylation for characteristic bands of methyl around 2832 cm^{-1} disappeared. The product of demethylation keeps high molecular weight and the polydispersity was sharp. Gel permeation chromatography (GPC) in THF: Number-average molecular weight (M_n), 15000; index of polydispersity (M_w/M_n), 1.61.

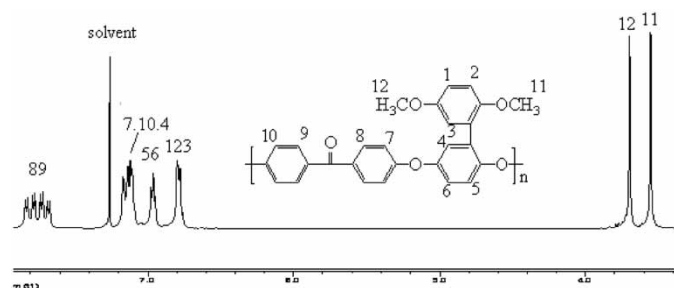


Fig. 3. 500 MHz $^1\text{H-NMR}$ spectrum of DMP-PEEK in CDCl_3 .

3.4 Structure and Property of Polymers

The two polymers show excellent solubility in original solvent at room temperature (Table 1). The good solubility could be attributed to the introduction of the bulky substituent, which disturbs the close packing of the polymer chains and leads to the increased free volume. DMP-PEEK was soluble in chloroform at room temperature whereas the DHP-PEEK was insoluble. The hydroxyl increases so that solubility of DHP-PEEK in aprotic polar solvents is less than in the weak polar solvents. All of the polymers are

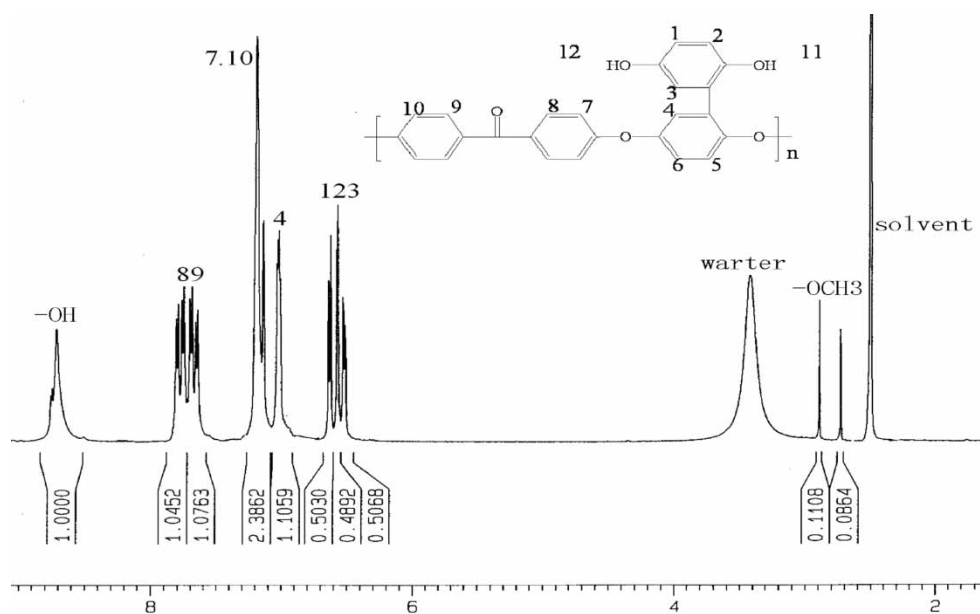


Fig. 4. 500 MHz $^1\text{H-NMR}$ spectrum of DHP-PEEK in DMSO-d_6 .

Table 1. Solubilities of polymers

Solubility	Chloroform	DMF	DMAC	NMP	THF	DMSO	Toluene
DMP-PEEK	++	++	++	++	++	++	-
DHP-PEEK	-	++	++	++	++	++	-

++ , soluble at room temperature; + , soluble on heating; - , insoluble.

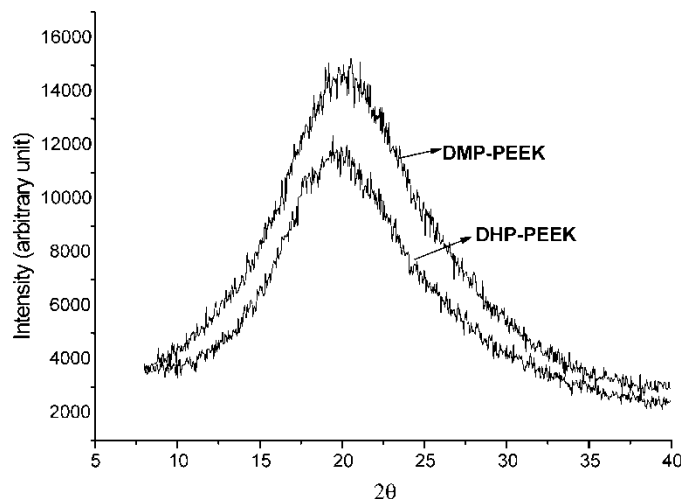


Fig. 5. Wide angle X-ray scattering curves of DMP-PEEK and DHP-PEEK.

amorphous. The X-ray spectra of polymers show a diffuse scattering peak with no crystallization peak for the introduction of the bulky substituents (Figure 5).

The glass transition temperature (T_g) and the thermal stability of the polymers have been investigated with differential scanning calorimetry (DSC) (Figure 6) and thermogravimetric analysis (TGA) (Figure 7) measurements under nitrogen. Both polymers, DMP-PEEK and DHP-PEEK, are amorphous polymers. The glass transition temperature (T_g) of DHP-PEEK (210°C) was higher than DMP-PEEK (150°C). The high T_g of this DHP-PEEK is interpreted in terms of the increase of hydroxyl groups. A thermogravimetric procedure of the DMP-PEEK was performed in two steps, corresponding to the degradation of dimethoxy group at 473°C and polymer skeleton at 629°C , respectively. It is shown that the methoxy groups trigger off the degradation of the poly(ether ether ketone)s (8). The thermogravimetric temperature of DHP-PEEK at 5% weight loss was at 310°C . As a result, introduction of the hydroxyl group results in a drop of thermal resistances. These differences were

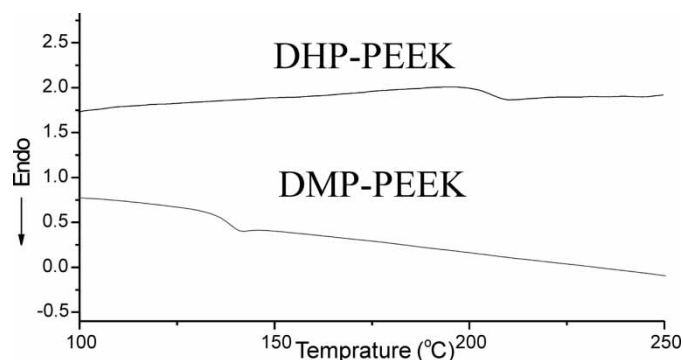


Fig. 6. DSC curves of DMP-PEEK and DHP-PEEK under nitrogen.

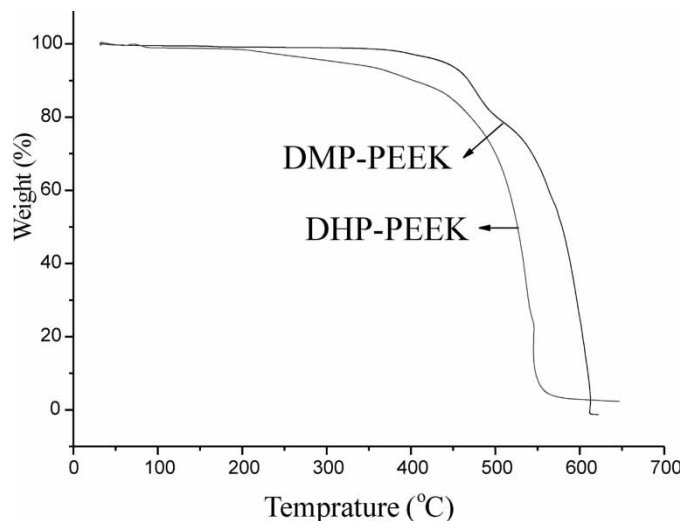


Fig. 7. TGA curves of DMP-PEEK and DHP-PEEK under air.

considered to be in agreement with the variety of the pendent part of the polymer. Upon heating, the oxidation of hydroxyl led to degradation.

4 Conclusions

A new methoxy-containing aromatic bisphenol monomer, (2,5-dimethoxy)phenylhydroquinone, was synthesized and characterized, which undergoes reactions with difluoro monomer to produce amorphous poly(ether ketone)s, that is soluble in original solvent at room temperature. The DHP-PEEK with good solubility with hydrophilicity solvent was obtained by the method of hydrolysis of methoxy group. The DHP-PEEK showed high glass transition temperature. Both of the polymers are amorphous.

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