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Synthesis of Poly(arylene ether ketone)s containing Unsymmetrical Pyridyl Ether Linkages

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Summary

New high molecular weight poly(arylene ether ketone)s were prepared from pyridine containing unsymmetrical dichloro monomers. Incorporation of unsymmetrical pyridyl ether linkages instead of phenylene ether linkages reduces the high crystallinity of parent poly(arylene ether ketone)s and provides enhanced solubility. Replacement of a single atom in the repeating units of polymers can efficiently change the physical properties of the resulting polymers. The pyridyl ether containing poly(arylene ether ketone)s showed outstanding thermal stability ($T_{d5} > 470$ °C).

Introduction

Poly(arylene ether ketone)s (PEEK's) are well-recognized high performance engineering thermoplastics with outstanding physical properties, including high modulus, toughness, and good thermal/chemical resistance [1-4]. The nucleophilic route has been known as the most general method to prepare various kinds of poly(arylene ether ketone)s. This involves generation of an ether linkage by a nucleophilic aromatic substitution (S_NAr) reaction as a polymer-forming reaction and uses dihalide monomers of which halides are activated by carbonyl groups at the para position. The best leaving groups for the polymerization are fluorine groups but chlorine or nitro leaving groups can be utilized as efficient leaving groups in some cases [5-9].

In spite of their excellent performance, the processing and even the synthesis of poly(arylene ether ketone)s has been limited because of their low solubility in common organic solvents resulting from their high crystallinity, which originates from the high packing tendency of ketone and phenyl ether linkages in the main-chain of poly(arylene ether ketone)s. Improved solubility and processability have been accomplished by the incorporation of meta-linkages, flexible linkages, and bulky substituents [10-14]. Most of the above approaches for amorphous poly(arylene ether ketone)s aimed at the reduction of several types of chain-chain interaction such as chain packing (e.g. crystallinity).

Here we report the synthesis of novel poly(arylene ether ketone)s with unsymmetrical pyridyl ether linkages (py-PEEK's). Py-PEEK's are structurally different from the corresponding phenyl ether containing polymers (PEEK's) from a point of view that only one carbon atom of each repeating unit is changed by a nitrogen atom. This one atom change is the least structural modification to parent PEEK's and the resulting py-PEEK's are isoelectric compared with PEEK's. It is interesting to see how much of the physical properties are affected by such a minimum structural modification of the repeating units of a polymer [15]. In addition, it is well known that polymers containing heterocyclic units in the main chain possess excellent thermal stabilities [16]. Therefore, incorporation of pyridyl ether linkages may induce least detrimental effects on the thermal properties of the polymer.

Experimental

Materials

6-Chloronicotinic acid and *t*-butylphenol were purchased from Aldrich Chemical Company. All the aromatic diols were also purchased from Aldrich Chemical Company and purified by recrystallization in benzene or toluene. *N*,*N*-Dimethylacetamide (DMAc) was dried over calcium hydride for 24 h and distilled under reduced pressure. Thionyl chloride was distilled by simple distillation and toluene was dried over sodium and distilled before use.

Instruments

FT IR spectra of the compounds were obtained with a Brucker EQUINOX-55 spectrophotometer using KBr pellet. NMR spectra of the synthesized compounds were recorded on Brucker Fourier Transform AVANCE 300 spectrometers. High-resolution mass (HR MS) spectra of the monomers and model compounds were obtained with a Jeol JMS-SX-102 mass spectrometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a TA 2200 thermal analyzer system at a heating rate of 10 ^{o}C/min in nitrogen. Molecular weights of polymers were determined by gel permeation chromatography using *o*-dichlorobenzene as an eluent at 85 ^{o}C with polystyrene standards.

Synthesis of 6-chloronicotinic acid chloride

6-Chloronicotinic acid (25.00 g, 158.7 mmol) was added to 175 mL of thionyl chloride. After reflux for 12 h, excess thionyl chloride was removed by the simple and subsequent vacuum distillation. The resulting bright brown solid was used without further purification.

*Synthesis of 5-(4-Chlorobenzoyl)-2-chloropyridine (**1**)*

6-Chloronicotinic acid chloride (5.00 g, 28.4 mmol) was added to 24 mL of chlorobenzene in nitrogen. Aluminum trichloride (13.3 g, 99.4 mmol) was added in small portion into the reaction mixture for 2 h. After stirring for 6 h, the reaction mixture was heated to 80 ^{o}C for 6 h. The crude reaction mixture was cooled and poured added to into 500 mL of distilled water. The excess chlorobenzene was removed by heating. The resulting solid was collected by filtration and dried in reduced pressure at 40 °C. The crude solid was sublimed under vacuum at 80 °C and recrystallized from toluene. Yield: 92 %. HR MS: m/z = 250.9905 [M$^+$], Calcd 250.9905 for $C_{12}H_7Cl_2NO$. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.70 (d, 1H), 8.05 (dd, 1H), 7.72 (d, 2H), 7.47 (m, 3H). ^{13}C NMR (75.1 MHz, $CDCl_3$): δ = 192.2, 153.6, 150.6, 140.4, 138.4, 134.7, 131.8, 131.6, 128.9, 124.4.

*Synthesis of 5-(4-t-Butylphenoxybenzoyl)-2-(4-t-butylphenoxy)pyridine (**2**)*

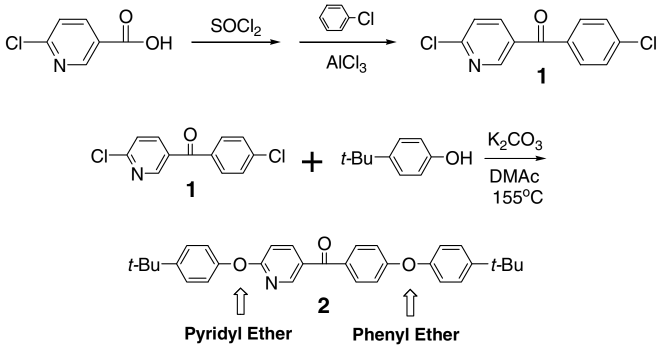
1 (0.50000 g, 1.9834 mmol), *t*-butylphenol (0.5959 g, 3.967 mmol), and potassium carbonate (0.658 g, 4.76 mmol) were added into a mixture of 4.4 mL of DMAc and 2 mL of toluene. The mixture was stirred mechanically at 155 °C while removing the toluene by azeotropic distillation. The reaction mixture was cooled to room temperature, acidified with 1 mL of acetic acid, and precipitated into water. The precipitate was collected by filtration and dried under vacuum. Yield: 95 %. HR MS: m/z = 479.2465 [M$^+$], Calcd 479.2460 for $C_{32}H_{33}NO_3$. ^{1}H NMR (300, MHz, DMSO-d_6): δ = 8.46 (d, 1H), 8.15 (dd, 1H), 7.77 (d, 2H), 7.43 (m, 4H), 7.10 (m, 7H), 1.26 (d, 18H, $-C(CH_3)_3$). ^{13}C NMR (75.1 MHz, $CDCl_3$): δ = 192.4, 165.2, 162.4, 153.1, 151.7, 150.2, 147.1, 146.9, 140.3, 132.5, 131.1, 128.9, 128.4, 128.1, 128.3, 121.1, 119.2, 117.5, 111.0, 42.5, 42.4, 30.9, 30.8.

Polymerization

Representative polymerization procedure is following for the synthesis of **P2**.
A three-neck flask equipped with a condenser was charged with **1** (0.5000 g, 1.983 mmol) and 4,4'-isopropylidenediphenol (0.4528 g, 1.983 mmol) in 3.8 mL of DMAc and 1.7 mL of toluene. The reaction mixture was heated into 155 °C while removing the toluene by azeotropic distillation. After polymerization for 12 h, the viscous polymerization mixture was cooled to room temperature, acidified with 1 mL of acetic acid, and precipitated into water. The white fibrous polymer was collected by filtration and dried under vacuum at 80 °C. Yield: 99 %. T_g: 153 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.56 (d, 1H), 8.16 (dd, 1H), 7.78 (d, 2H), 7.30 (m, 4H), 7.09 (m, 7H). ^{13}C NMR (75.1 MHz, $CDCl_3$): δ = 192.5, 165.8, 161.9, 153.2, 151.2, 150.4, 147.3, 146.9, 140.9, 132.2, 131.4, 128.6, 128.4, 128.3, 128.2, 120.8, 119.6, 117.2, 111.1, 42.4, 30.9.

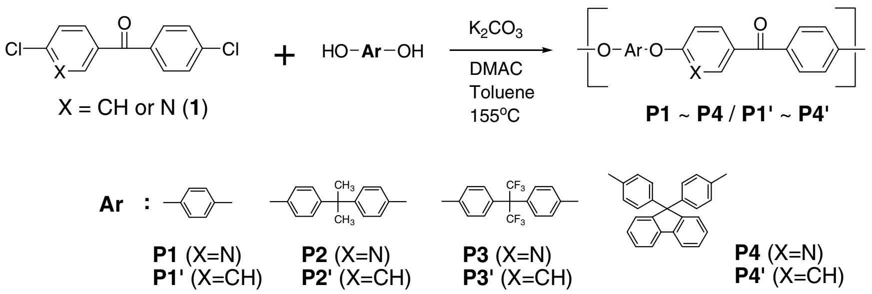
Results and Discussion

Unsymmetrical pyridine containing dichloro ketone monomer (**1**) was synthesized by the Friedel-Crafts acylation of nicotinic acid chloride with excess chlorobenzene (Scheme 1). The structure of the monomer was confirmed by FT IR and NMR spectroscopy.
To investigate the feasibility of polymerization, model reaction was conducted with *t*-butylphenol in DMAc. The model compound **2** was obtained in quantitative yield within 2 h at 155 °C (Scheme 1). The structure of model compound **2** was confirmed by ^{1}H NMR and ^{13}C NMR. All expected 22 carbons originated from the unsymmetric structure of **2** were appeared in ^{13}C NMR.



Scheme 1. Synthesis of monomer (**1**) and model compound (**2**)

The successful result of the model reaction prompted us to perform the polymerization with various aromatic diols. The monomer **1** was polymerized with various aromatic diols, according to the conventional poly(arylene ether) synthesis, with K_2CO_3 as a base in DMAc (Scheme 2). The solid content was maintained around 25 wt.-%. The weight average molecular weights of the polymers determined by GPC with polystyrene standards were over 30,000 in all cases except **P1**, which is insoluble in nearly all organic solvents.



Scheme 2. Polymerization of **1** with various aromatic diols

The structure of the polymers was confirmed with FT IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. FT IR spectra of the monomers showed the characteristic peaks of carbonyl and pyridine ring and those peaks were preserved in FT IR spectra of the polymers. Strong aryl ether stretching peak was also observed. ^{1}H NMR and ^{13}C NMR spectra of the polymers showed all expected peaks in all cases.

There are totally 3 different repeating units (H-H, H-T, T-T) in the polymer main chain because pyridine-containing monomer **1** is unsymmetrical (AA' type monomer). The three repeating units were well resolved in ^{13}C NMR, thus enabling calculation of the structural regularity (s) of polymers (Figure 1) [17]. Ideally, AA' + BB polymerization must induce random configuration of such repeating units. The calculated probability for the structural regularity from ^{13}C NMR spectrum of **P2**, is 0.52, which is an almost same value with the theoretical value of random configurations (s = 0.50).

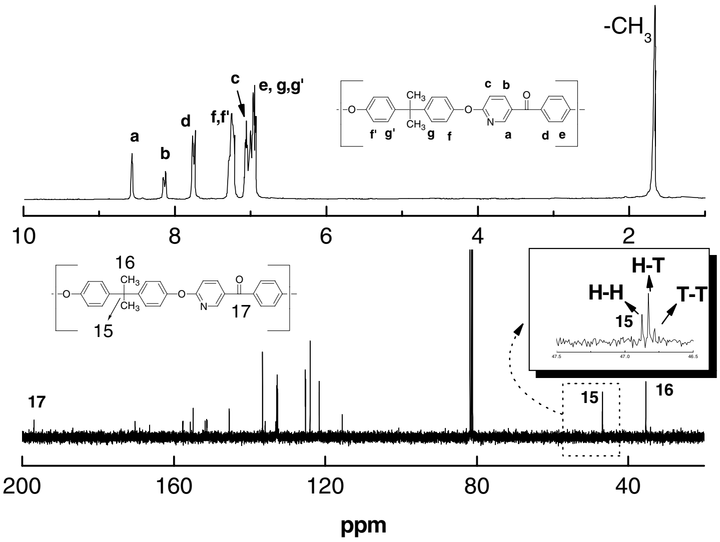


Figure 1. ^{1}H and ^{13}C NMR Spectra of polymer **P2** (at 25 °C in $CDCl_3$)

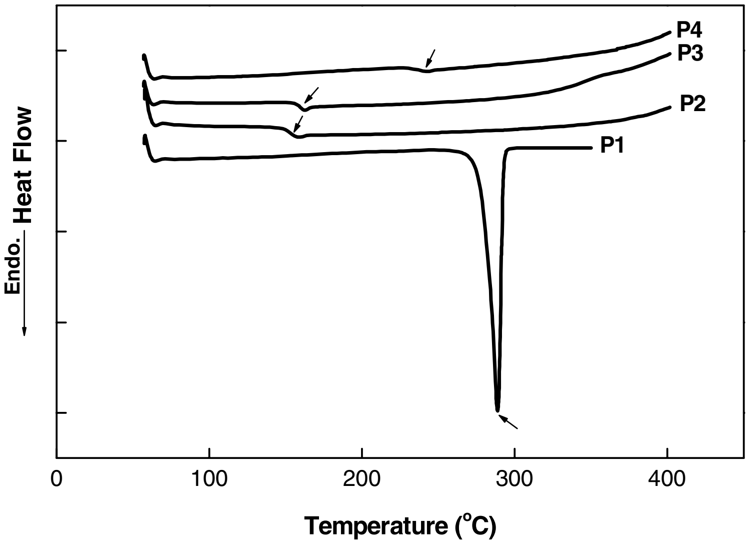


Figure 2. DSC of polymers

The polymers were quite soluble in chlorinated solvents like chloroform and 1,2-dichlorobenzene but less soluble in aprotic polar solvents such as DMF and DMSO without heating. Among these polymers, solubility of **P3** is better than others. **P3** is soluble even in DMF and DMSO at room temperature. Transparent, pale yellow and flexible films were prepared by solution casting from a chloroform solution of the polymers.

Table 1. Results of polymerization

Polymer	Yield (%)	M_n [a]	M_w [a]	M_w/M_n [a]
P1	94.5	---[b]	---	---
P2	99.0	19,700	33,700	1.7
P3	99.9	9,800	29,900	3.1
P4	99.8	35,200	67,400	1.9

[a] determined by GPC using *o*-dichlorobenzene as eluent at 85 °C with polystyrene standards;
[b] not measured

Table 2. Properties of polymers

Py-PEEK	T_g [a] (°C)	T_m [a] (°C)	T_{d5} [b] (°C)	**PEEK**	T_g [a] (°C)	T_m [a] (°C)
P1	---[c]	288	471	**P1'**	144[d]	335[d]
P2	153	---	472	**P2'**	155[e]	248[e]
P3	159	---	495	**P3'**	175[e]	---
P4	238	---	492	**P4'**	252[e]	---

[a] Measured by DSC with a heating rate of 10 °C/min in nitrogen; [b] 5% weight loss temperature measured by TGA with a heating rate of 10 °C/min in nitrogen; [c] Not detected; [d] See ref. [1];
[e] See ref. [3]

Table 1 and Table 2 summarize the physical properties of the pyridine containing polymers compared with the corresponding polymers without pyridine moiety. The glass transition temperatures of py-PEEK's are similar to those of the phenyl ether analogues. However, by replacing one phenyl ring with pyridine ring, **P2** becomes amorphous while the corresponding PEEK **P2'** is crystalline. But in the case of **P1**, the crystalline nature of PEEK (**P1'**) was not changed so much and polymer **P1** showed clear melting transition temperature at 288 °C. As expected, the glass transition temperature of **P4** with bulky groups (238 °C) is higher than that of **P2** and **P3** (153 °C and 159 °C) (Figure 2). These results indicates that minor modification such as substitution of only one atom in the polymer repeating unit can induce change of physical properties of parent polymers. We attribute this to the reduced chain packing of py-PEEK by the change of configuration of ether linkages. General aryl ether linkages of PEEK have C-O-C bond angle of 123 °C, which is almost same with the C-(C=O)-C bond angle of the benzophenone moiety [18,19]. Substitution of single nitrogen atom for the carbon atom next to the aryl ether linkage can change the configuration of this ether linkage. Lone pair repulsion between oxygen and nitrogen of pyridyl ether linkage can twist the pyridyl ring vertically to the phenyl ring, thus hampering the efficient chain packing of polymers. Thermal analysis showed that the polymers have high thermal stability with 5% weight loss temperatures over 450 °C. The incorporation of pyridine ring instead of phenyl is not detrimental to the thermal stability of PEEK's while increasing solubility and processability of them. The pyridyl groups in the polymer backbone can be used for further functionalization.

Conclusions

New high molecular weight poly(arylene ether ketone)s were prepared from the pyridine containing unsymmetrical dichloro monomer. Incorporation of unsymmetrical pyridyl ether linkages instead of phenylene ether linkages reduces the high crystallinity of parent poly(arylene ether ketone) and provides enhanced solubility. The modification of single atom in the repeating unit of polymers can efficiently change the physical properties of the resulting polymers. The polymers showed outstanding thermal stability and good film-forming properties. Incorporation of unsymmetrical pyridyl ether linkages into other polymer systems is in progress.

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