

Synthesis and Characterization of Polybenzimidazoles Containing Perfluorocyclobutane Groups for High-temperature Fuel Cell Applications

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Abstract: This paper describes the preparation and characterization of two kinds of fluorinated polybenzimidazole (PBI)s which can be potentially used for phosphoric acid-doped, high-temperature polymer electrolyte membrane fuel cells. Two kinds of perfluorocyclobutane (PFCB)-containing monomers were prepared via following synthetic steps; after fluoroalkylation of methyl 3-(hydroxy) benzoate and methyl 4-(hydroxy) benzoate with 1,2-dibromotetrafluoroethane and subsequent Zn-mediated dehalogenation, these compounds were cyclodimerized at 200°C affording the ester-terminated monomers containing PFCB ether groups. The synthesized intermediates and monomers were characterized using FT-IR, ¹H-NMR, ¹⁹F-NMR, and mass spectroscopy. The fluorinated PBIs were then successfully prepared through the solution polycondensation of the monomers and 3,3'-diaminobenzidine in polyphosphoric acid. Compared with traditional PBI, the glass transition temperatures of the fluorinated PBIs were obtained at 262°C and 269°C which are lower than that of PBI and their initial degradation temperatures were still high over 400°C under nitrogen. The fluorinated PBIs showed higher d-spacing values and improved solubility in several organic solvents as well as phosphoric acid, which confirmed they could be good candidates for the high temperature fuel cell membranes.

Keywords: fluorinated polybenzimidazole, perfluorocyclobutane, phosphoric acid-doped, high-temperature polymer electrolyte membrane fuel cells

1. Introduction

PBIs are amorphous thermoplastic polymers obtained by the polycondensation of aromatic tetraamines and aromatic diacid derivatives [1,2]. Since their backbone is composed of fully rigid aromatic compounds, PBIs exhibit high thermal stability, non-flammability, and excellent chemical resistance [1-3]. These properties have enabled the PBIs to be useful in many applications such as fibers, fabrics, molded shapes, parts for semiconductor and hollow fibers for reverse osmosis and so on [3-5].

Recently, polymer electrolyte membrane fuel cells

have become one of the key technologies leading the 21st century. Especially, the high-temperature polymer electrolyte fuel cells have received extensive attention because of enhanced cell efficiency low CO catalyst poisoning at high operation temperature above 140°C [6-8]. However, although PBIs possess the above superior merits, they has poor solubility and infusibility due to the rigidity and strong interaction among their chains, thus further membrane fabrication process was restricted severely; they should be cast on high temperature above 150°C in phosphoric acid. Some significant studies have been carried out to overcome these fabrication problems [8-13]. These efforts include the modification of PBI through copolymerization and block copolymerization [8,9]. Reynolds *et al.* in

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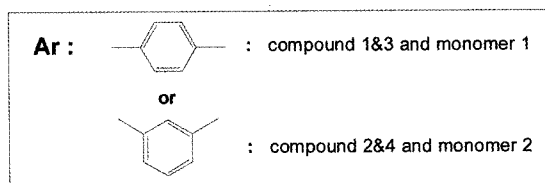
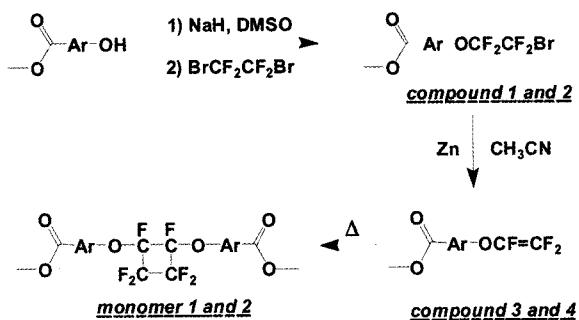


Fig. 1. Schematic representation of the preparation of PFCB-containing monomers.

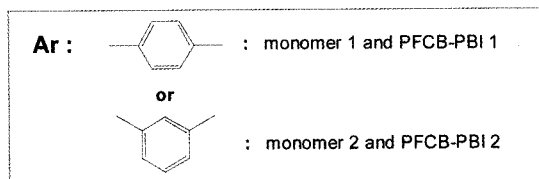
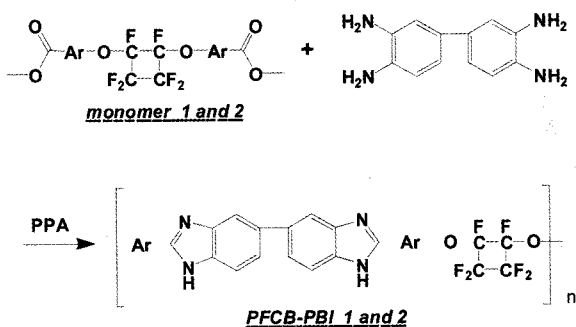


Fig. 2. Schematic representation of the preparation of PFCB-PBIs.

troduced sulfonated side chains onto the PBI backbone that imparted improved solubility to the derivative polymer [10,11]. Some efforts were also expended to produce modified PBIs with sulfonic acid and alkyl substituents [12,13].

On the other hand, D. A. Babb and coworkers developed a new synthetic route to PFCB-containing polymers [14], where PFCB rings enhanced the solubility and processability without losing chemical and thermal

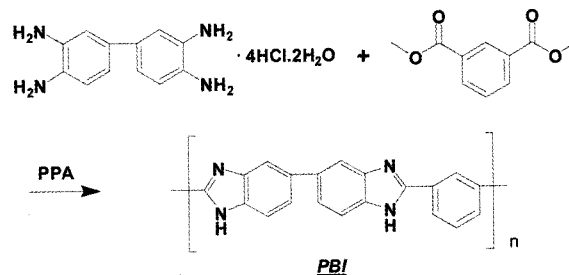


Fig. 3. Schematic representation of the preparation of non-fluorinated PBI.

stabilities. Many other PFCB-containing polymers have been synthesized and exhibited excellent properties such as low dielectric constant, low refractive index, low surface energy, good thermal/oxidative stability, excellent processability, and optical transparency [15-20]. In this respect, the incorporation of the PFCB group into rigid PBI might improve the solubility and processability without sacrificing the advantages of PBIs. To our knowledge, the PBIs with PFCB rings have not been reported yet in the polymer-related journals. Here, we have developed new PBIs, in which the PFCB group is covalently combined to the benzimidazole moiety in the polymer backbone through the ether linkage. Two kinds of compounds containing the trifluorovinyl group were prepared and cyclodimerized to give the diester monomers with the PFCB group and the synthetic procedures are depicted in Fig. 1. Then, the diester monomers were condensed with 3,3'-diaminobenzidine in polyphosphoric acid (PPA) to synthesize the PFCB-containing PBIs (PFCB-PBIs) via solution polycondensation as shown in Fig. 2. As a reference material, poly-*m*-phenylenebenzimidazole (PBI) was prepared as described in the literature [2] and the synthetic procedure is depicted in Fig. 3. Spectroscopic and thermal characterizations and solubility tests were carried out with the prepared monomers and polymers.

2. Experimental

2.1. Materials

All the reagents and solvents used for synthesis were purchased from Aldrich chemical Co. Dimethylsulfo-

xide (DMSO), acetonitrile and 1, 2-dibromotetrafluoroethane (DBTFE) were dried over CaH_2 in an atmosphere of dry nitrogen. Zinc (granule, 20 mesh, 99.8 + %) was activated with 0.1 M hydrochloric acid, washed with water and acetone, and then dried at 100°C under reduced pressure for 24 h. All of other reagents and solvents were used as received.

2.2. Instrumentation

Nuclear magnetic resonance (NMR) spectra ($^1\text{H-NMR}$ and $^{19}\text{F-NMR}$) and infrared (IR) spectra were obtained on a Bruker DRX-300 FT-NMR Spectrometer at 300 MHz using tetramethylsilane as an internal standard material and on a Bio-Rad Digilab FTS-165 FT-IR Spectrometer, respectively. With a heating rate of $10^\circ\text{C}/\text{min}$ in a nitrogen atmosphere, glass transition temperatures (T_g) and initial degradation temperatures (T_d) were monitored by a Different Scanning Calorimeter (TA Instruments DSC 2910) and by a thermogravimetric analyzer (TA Instruments DMA 2980), respectively. Intrinsic viscosity (η_{int}) was measured in *N,N*-dimethylacetamide (DMAc) using a Cannon-Fenske viscometer [21]. Mass spectrometric analysis data were recorded on a Micromass AutoSpec Mass Spectrometer (brand name). The d-spacing of polymers was examined by an X-ray diffractometer (D/MAX-2200V X-ray diffractometer) equipped with Cu tube and graphite monochromator.

2.3. Synthesis of PFCB-containing Monomers

2.3.1. Methyl 4-(2-bromotetrafluoroethoxy) Benzoate (Compound 1)

In a three-necked round bottom flask equipped with a magnetic stirrer, a dropping funnel and a nitrogen gas bubbler, sodium hydride (60% dispersed in mineral oil) (4.8 g, 0.2 mol) was suspended in DMSO (400 mL). Methyl 4-(hydroxy) benzoate (0.2 mol) was subsequently added to the suspension slowly under nitrogen flow while magnetically stirred at room temperature for 2 h. The mixture was then cooled in ice bath and DBTFE (52 g, 0.2 mol) was added dropwise to the reaction mixture. The mixture was allowed to

warm to room temperature and stirred for 16 h. The mixture was then poured into distilled water and extracted with ethyl acetate three times. The combined organic layers were dried over magnesium sulfate and the solvent was evaporated. The resulting, slightly yellowish oil was chromatographically purified on a silica gel column using *n*-hexane and ethyl acetate as the eluent to yield 48.3 g of pure compound (73%). IR (KBr, cm^{-1}): Ar (1608, 1506); C=O (1730); C-O, C-F (1283, 1206, 1167, 1105); Ar (808, 758). $^1\text{H-NMR}$ (CDCl_3 , δ in ppm): 3.93 (s, 3H, OCH_3), 7.28~8.11 (various m, 4H, CH arom.). $^{19}\text{F-NMR}$ (CDCl_3 , δ in ppm): -86.48 (s, 2F, $-\text{CF}_2\text{CF}_2\text{Br}$), -68.62 (s, 2F, $-\text{CF}_2\text{CF}_2\text{Br}$).

2.3.2. Methyl 3-(2-bromotetrafluoroethoxy) Benzoate (Compound 2)

Compound 2 was prepared through the same preparation method of compound 1 except that methyl 3-(hydroxy) benzoate (30.4 g, 0.2 mol) was used instead of methyl 4-(hydroxy) benzoate. 43 g of pure compound was obtained (65%). IR (KBr, cm^{-1}): Ar (1590, 1488); C=O (1731); C-O, C-F (1299, 1274, 1206, 1163, 1132, 1106). $^1\text{H-NMR}$ (CDCl_3 , δ in ppm): 3.95 (s, 3H, OCH_3), 7.42~8.01 (various m, 4H, CH arom.). $^{19}\text{F-NMR}$ (CDCl_3 , δ in ppm): -86.52 (s, 2F, $-\text{CF}_2\text{CF}_2\text{Br}$), -68.64 (s, 2F, $-\text{CF}_2\text{CF}_2\text{Br}$).

2.3.3. Methyl 4-(trifluorovinylloxy) Benzoate (Compound 3)

Compound 1 (33.1 g, 0.1 mol) was added to a solution of activated zinc powder (7.2 g, 0.11 mol) and acetonitrile (300 mL) in a three-necked flask equipped with a reflux condenser, a nitrogen gas bubbler and a magnetic stirrer. The mixture was refluxed for 16 h, filtered and concentrated under reduced pressure. The raw product was then chromatographed on a silica gel column using *n*-hexane and ethyl acetate as the eluent to obtain 19.7 g of pure compound (85%). IR (KBr, cm^{-1}): $-\text{CF}=\text{CF}_2$ (1835); Ar (1607, 1504); C=O (1728). $^1\text{H-NMR}$ (CDCl_3 , δ in ppm): 3.92 (s, 3H, OCH_3), 7.14~8.10 (various m, 4H, CH arom.). $^{19}\text{F-NMR}$ (CDCl_3 ,

δ in ppm): -118.2 (1F, dd, cis-CF=CF₂), -124.8 (1F, dd, trans-CF=CF₂), -134.2 (1F, dd, -CF=CF₂).

2.3.4. Methyl 3-(trifluorovinyl)oxy) Benzoate (Compound 4)

Compound 4 was prepared through the same preparation method of compound 3 except that compound 2 (33.1 g, 0.1 mol) was used instead of compound 1. 13.9 g of pure compound was obtained (60%). IR (KBr, cm⁻¹): -CF=CF₂ (1824); Ar (1581, 1477); C=O (1720). ¹H-NMR (CDCl₃, δ in ppm): 3.95 (s, 3H, OCH₃), 7.42~8.01 (various m, 4H, CH arom.). ¹⁹F-NMR (CDCl₃, δ in ppm): -119.8 (1F, dd, cis-CF=CF₂), -126.7 (1F, dd, trans-CF=CF₂), -134.9 (1F, dd, cis-CF=CF₂).

2.3.5. 1,2-bis(4-methylesterphenoxy)tetrafluorocyclobutane (Monomer 1)

Compound 3 (11.6 g, 0.05 mol) was heated at 200°C for 16 h under an atmosphere of nitrogen. The raw product was then chromatographed on a silica gel column using *n*-hexane with ethyl acetate as the eluent to yield 11.1 g of pure compound (96%). IR (KBr, cm⁻¹): Ar (1608, 1507); C=O (1723); hexafluorocyclobutane (961). [M]⁺: Calcd. 464.31; Found 464. ¹H-NMR (CDCl₃, δ in ppm): 3.93 (s, 6H, OCH₃), 7.30~7.89 (various m, 8H, CH arom.). ¹⁹F-NMR (CDCl₃, δ in ppm): -127.1, -128.5, -129.3, -129.9, -130.7, -131.5, -131.6, -132.1, -133.2.

2.3.6. 1,2-bis(3-methylesterphenoxy)tetrafluorocyclobutane (Monomer 2)

Monomer 2 was prepared through the same preparation method of monomer 1 except that compound 4 (11.6 g, 0.05 mol) instead of compound 3 was used. 11.1 g of pure compound was obtained (96%). IR (KBr, cm⁻¹): Ar (1579, 1479); C=O (1716); hexafluorocyclobutane (950). [M]⁺: Calcd. 464.31; Found 464. ¹H-NMR (CDCl₃, δ in ppm): 3.94 (s, 6H, OCH₃), 7.31~7.89 (various m, 8H, CH arom.). ¹⁹F-NMR (CDCl₃, δ in ppm): -127.1, -128.5, -129.3, -129.9, -130.7, -131.5, -131.6, -132.1, -133.2.

2.4. Preparation of PBIs

2.4.1. Non-fluorinated PBI

As a reference material, poly-*m*-phenylenebenzimidazole was prepared by the solution polycondensation from 3,3'-diaminobenzidine tetrahydrochloride and dimethyl isophthalate in PPA according to the synthetic scheme in Fig. 3 described in the literature [2].

2.4.2. PFCB-containing PBIs (PFCB-PBIs)

2.4.2.1. PFCB-PBI 1

To a 250 mL three-necked flask, PPA (200 g), monomer 1 (9.29 g, 0.02 mol) and 3,3'-diaminobenzidine (4.29 g, 0.02 mol) were added. The mixture was heated to 190°C while mechanically stirred for 24 h under nitrogen. The polymer prepared was isolated by pouring the hot mixture into water. It was then washed with water by decantation, and transferred into an excess of saturated sodium hydrogen carbonate aqueous solution overnight. The filtered polymer was washed thoroughly with water, methanol and dried under reduced pressure. IR (KBr, cm⁻¹): hexafluorocyclobutane (957); N=C (1614); N-H (3432). ¹H-NMR (DMSO-d₆, δ in ppm): 13.02 (s, 2H, NH), 7.32~8.26 (various m, 14H, CH arom.). ¹⁹F-NMR (DMSO-d₆, δ in ppm): -127.1~-132.1.

2.4.2.2. PFCB-PBI 2

PFCB-PBI 2 was prepared through the same preparation method of the PFCB-PBI 1 except that monomer 2 (9.29 g, 0.02 mol) instead of monomer 1 was used. IR (KBr, cm⁻¹): hexafluorocyclobutane (945); N=C (1604); N-H (3422). ¹H-NMR (DMSO-d₆, δ in ppm): 13.07 (s, 2H, NH), 7.35~8.23 (various m, 14H, CH arom.). ¹⁹F-NMR (DMSO-d₆, δ in ppm): -127.1~-133.2.

3. Results and Discussion

3.1. Monomer Synthesis

As shown in Fig. 1, the PFCB-containing monomers were prepared through three synthetic steps, that is, fluoroalkylation, Zn-mediated elimination, and thermal

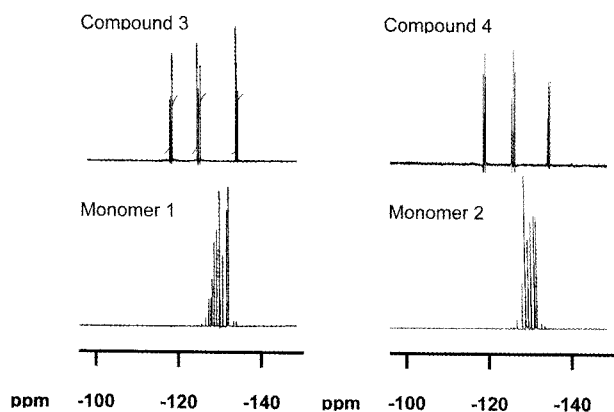


Fig. 4. ^{19}F -NMR spectra of trifluorovinyl- and PFCB-containing compounds and PFCB-containing monomers.

cyclodimerization. All the compounds and monomers synthesized were purified by column chromatography using silica gel as the stationary phase and mixtures of *n*-hexane and ethyl acetate as the eluting solvent. In the case of the fluoroalkylation reaction, compound 1 and 2 were prepared from phenolic ester materials and DBTFE in DMSO at 15~35°C for 16 h. NaH as a deprotonating agent was used instead of commonly used KOH as shown by D. Y. Kim *et al.* [19] because KOH generates water which gives rise to the formation of a by-product containing a tetrafluoroethyl ether group (-OCF₂CF₂H) and should be removed for the high yield of products as described elsewhere [14,16].

The reactions of compound 1 and 2 with activated zinc granules in acetonitrile yielded the trifluorovinyl-terminated intermediates, that is, compounds 3 and 4, respectively. Since this Zn-mediated elimination also causes the formation of the by-product, all the chemicals used in the synthesis were carefully dried. These compounds were then cyclodimerized at high temperature to afford the ester-terminated PFCB-containing monomers in high yields. The thermal [$2\pi + 2\pi$] cyclodimerization of trifluorovinyl compounds is a well-known reaction in which a mixture of *cis*- and *trans*-1,2-disubstituted PFCB rings is formed in a head-to-head orientation via the formation of the stable biradical intermediate and subsequent ring closure [14, 20].

Fig. 4 shows the ^{19}F NMR spectra of the trifluorovinyl-terminated compounds and PFCB-containing monomers. The typical peaks from the trifluorovinyl group are observed in three different regions around -118~-120, -124~-127, and -134~-135 ppm. On the other hand, after cyclodimerization, new multiple peaks are generated around -127~-134 that are contributed to the *cis* and *trans* substituted PFCB rings [22] and the peaks from the trifluorovinyl group are disappeared. Each structure of compounds and monomers was also ascertained by FT-IR. The spectra of compound 3 and 4 show the sharp bands at 1,835 and 1,824 cm^{-1} which are the typical signal of the trifluorovinyl group, while those of monomer 1, 2 exhibit the bands at 961 and 950 cm^{-1} which represent the PFCB unit.

3.2. Synthesis of PFCB-PBIs

Two kinds of PFCB-PBIs were prepared by the solution polycondensation from 3, 3'-diaminobenzidine with monomer 1 and 2 as illustrated in Fig. 2. The monomer 1 and 2 were well soluble in PPA at the reaction temperature. At first, the polymerization reactions proceeded in homogeneous solutions and gradually became viscous to produce heterogeneous dark brown mixtures. The pouring of the hot mixtures into water was effective to isolate the polymers. The filtered polymers were washed with water by decantation, dipped in a saturated sodium hydrogen carbonate aqueous solution to remove residual acid, and washed thoroughly with water until the filtrate became neutral.

The structures of the PFCB-PBIs were confirmed by FT-IR as presented in Fig. 5. The PFCB unit is represented by the peaks at 957 (PFCB-PBI 1) and 945 cm^{-1} (PFCB-PBI 2). The presence of the peaks from N=C at 1,614 (PFCB-PBI 1), 1,605 cm^{-1} (PFCB-PBI 2) and N-H at 3,414 (PFCB-PBI 1), 3,425 cm^{-1} (PFCB-PBI 2) ascertains the benzimidazole structure. The absence of the characteristic carbonyl absorption peaks between 1,780 and 1,650 cm^{-1} suggests the complete cyclization of the imidazole rings. The structural

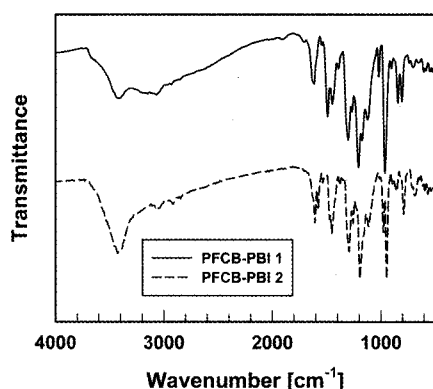


Fig. 5. FT-IR spectra of PFCB-PBIs.

Table 1. Physical Properties of PFCB-PBIs

Polymer	η_{int}	D-spacing (Å)	T_g (°C) ^a	T_d (°C) ^b
PFCB-PBI 1	0.52	5.09	262°C	409°C
PFCB-PBI 2	0.41	4.90	269°C	411°C
Non-fluorinated PBI	0.73	4.46	-	-

^a Measured by DSC at 10°C/min under a nitrogen atmosphere.

^b Measured by TGA at 10°C/min under a nitrogen atmosphere.

confirmation of the resultant polymers was also supported by NMR spectroscopy data. In the ¹H-NMR, the spectra show multiple peaks from the aromatic rings around 7.3~8.3 ppm. The peaks around 13 ppm indicate the NH group in the imidazole moiety. In the ¹⁹F-NMR, the peaks from the PFCB group are shown around -127.1~-133.2 ppm like the PFCB-containing monomers.

Intrinsic viscosity (η_{int}) of the polymers synthesized was measured from the equation (1) using a Cannon-Fenske viscometer at 30°C in DMAc with a concentration of 0.5 g/dL [21] :

$$\eta_{int} = \frac{\sqrt{2(\eta_{sp} - \ln \eta_{rel})}}{c} \quad (1)$$

where c is 0.5 g/dL, η_{sp} and η_{rel} represent the specific viscosity and relative viscosity, respectively.

As shown in Table 1, the intrinsic viscosity values are 0.52 dL/g for the PFCB-PBI 1 and 0.41 dL/g for the PFCB-PBI 2, which indicates that the molecular weights of the PFCB-PBIs are high enough for the

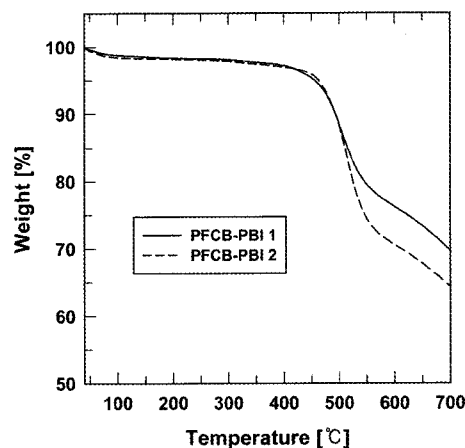


Fig. 6. Thermograms of PFCB-PBIs under a nitrogen atmosphere at a heating rate of 10°C/min.

preparation of tough polymer films.

3.3. Thermal Properties of PFCB-PBIs

The thermal stability of the PFCB-PBIs was evaluated by TGA under a nitrogen atmosphere and the results are presented in Fig. 6 and Table 1. The initial weight losses of ca. 1~2% are observed up to 100°C due to the in situ evaporation of the residual water which is bound to the hygroscopic imidazole moiety in the polymers.

The polymers display good thermal stability and no significant weight loss is detected until abrupt decomposition occurs above 400°C, which also guarantees the complete closure of the imidazole rings.

The T_g values of the PFCB-PBIs from DSC analysis are shown in Table 1. The values are 262°C for the PFCB-PBI 1 and 267°C for the PFCB-PBI 2, while the non-fluorinated PBI has a higher T_g around 430°C. The decreased T_g values of the PFCB-PBIs are ascribed to the presence of the flexible PFCB ether moiety. According to the literatures, the T_g values of 1,3 and 1,4-phenylene perfluorocyclobutyl ether polymers are 32 and 41°C, respectively [19,23,24]. Thus the introduction of the flexible PFCB ether moiety into the rigid PBI allows the movement of molecular segments to be easier in relatively low temperatures, resulting in the lowered T_g values.

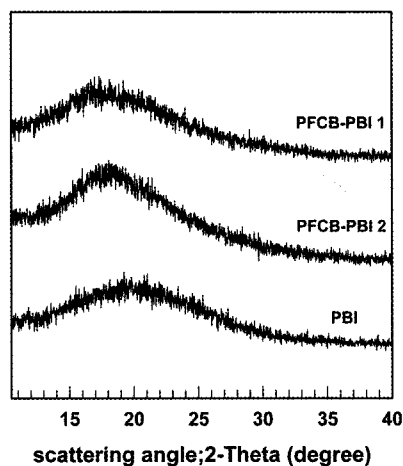


Fig. 7. Wide-angle X-ray diffractograms of non-fluorinated PBI and PFCB-PBIs.

3.4. X-ray Diffraction of PFCB-PBIs

The d-spacing of polymer measured from wide-angle X-ray scattering is often interpreted in terms of the average intermolecular distance of polymer matrix. The d-spacings of the PFCB-PBIs were obtained using Bragg's equation (2) :

$$\lambda = 2d \sin \theta \quad (2)$$

where λ is the wavelength (1.54 Å), d and θ represent the d-spacing and scattering angle, respectively.

Fig. 7 and Table 1 show the wide-angle X-ray diffractograms and the resulting d-spacing values of the polymer films prepared by solution casting. The broad peaks in the diffractograms indicate that the three samples have amorphous structures. Compared with the non-fluorinated PBI, the PFCB-PBIs show larger d-spacing values because of the presence of the flexible and bulky PFCB ether moiety in the polymer backbone chains. The bulkiness of the PFCB moiety is ascribed to the bulky butane ring with six fluorine

atoms, which increases the distance among molecular chains. In addition, due to the flexibility of the PFCB ether moiety the general mobility of polymer chains increases as described above, thus the free volume of the polymers increases resulting in the increased d-spacing.

3.5. Solubility of PFCB-PBIs

The solubility behavior of the PFCB-PBI polymers in various organic solvents was examined. Generally PBIs are difficult to dissolve due to the strong inter-chain hydrogen bond and the strong polarity of the imidazole rings [13]. As summarized in Table 2, the PFCB-PBIs showed improved solubility compared with the non-fluorinated PBI. The non-fluorinated PBI is soluble in polar aprotic DMAc, 1-methyl-2-pyrrolidone (NMP), and DMSO as well as phosphoric acid. It is partially soluble in *N,N*-dimethylformamide (DMF) but insoluble in tetrahydrofuran (THF) at room temperature. On the other hand, the PFCB-PBI 1 is soluble in DMF and the PFCB-PBI 2 is readily dissolved in THF which is a non-solvent for the non-fluorinated PBI, which indicates that fibers and membranes can be easily prepared using solution casting of the PFCB-PBIs.

The improved solubility of the PFCB-PBIs is attributed to the weaker interaction among their chains. It should be noted that the PFCB moiety is hydrophobic and the general polarity of the polymers decreased resulting in the weakened hydrogen bonding among polymer chains. Moreover, the increased distance among polymer chains leads to the weakened chain interaction, which also improves the solubility of polymers. The increased solubility of fluorinated PBIs indicates that the new PFCB ring-based PBIs prepared would be the good candidates for phosphoric acid doped high-

Table 2. Solubility of PFCB-PBIs

Polymer	DMAc	NMP	DMSO	DMF	THF	Acetone	CHCl ₃
PFCB-PBI 1	O	O	O	O	△	△	×
PFCB-PBI 2	O	O	O	O	O	△	×
Non-fluorinated PBI	O	O	O	△	×	×	×

※ O: denotes soluble at room temperature; △: denotes partially soluble; ×: denotes insoluble.

temperature polyelectrolyte composite membranes for fuel cell applications. Further studies on such areas with the PFCB-PBIs are going on in our laboratory.

4. Conclusions

We have prepared two newly fluorinated PBIs via the solution polycondensation of two PFCB-containing monomers and 3,3'-diaminobenzidine in PPA for high temperature polyelectrolyte membrane fuel cells. The PFCB-containing monomers were prepared through fluoroalkylation, dehalogenation, and cyclodimerization. The fluorinated PBIs showed excellent thermal stability with high T_d values over 400°C and their T_g values were 262 and 267°C, which were lower than that of the non-fluorinated. The PFCB-PBIs were dissolved in various common solvents as well as phosphoric acid, thus showed improved solubility compared with the non-fluorinated PBI. The new fluorinated PBIs could be potentially applied to the high temperature fuel cell membranes.

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