DOCTORAL DISSERTATION

STUDY ON PREPARATION OF HIGH PERFORMANCE POLYMERS DERIVED FROM BIOMASS

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INTRODUCTION AND THE AIM OF THIS STUDY

INTRODUCTION

The origin of polymer industries was derived from utilization of natural high polymers such as wood, resin, rubber and so on. The polymers were used before the early 1930s that its presence had been demonstrated. For instance, vulcanization of natural rubbers, reforming of cellulose and preparation of artificial silk so called rayon were performed in 1800s. [1] Since the early 1930s, many kinds of polymers have been artificially synthesized. At the beginning, nylons were intentionally synthesized by W. H. Carothers et al in the USA and vinyl polymers were did by the German company. [1] After that, appearance of synthetic rubbers, fibers and resins has encouraged the developments of petrochemical industry, synthetic organic chemistry, organometallic chemistry and catalytic chemistry which were the basis of polymer chemistry. The growth of these related fields promoted the development of new polymers. Polymers were classified into two groups by W. H. Carothers, which were condensation polymers and addition polymers. [2-17] P. J. Flory classified them again based on their formation mechanisms. [1, 18-25] Condensation polymers are formed by the step growth polymerization, which proceeds in incremental steps by the condensation reaction between functional groups of monomers with eliminating small molecules such as H₂O. In contrast, addition polymers were done by the chain growth reaction with the addition of active species.
formed by initiator to monomers. In general, step growth polymerization such as polycondensation can afford enormous types of polymers with changing the monomer species.

As development of polymer industry, the polymers were classified into two groups on the basis of their usage. One is the thermoplastic polymers and another is the thermosetting polymers. Furthermore, the thermoplastic polymers were classified into commodity plastics, engineering plastics and super engineering plastics. [26] Super engineering plastics have been called high performance polymers. Some of structures of them are shown in Figure 1. They possess aromatic rings mainly with a series of functional groups such as ester, amide, ether, ketone groups, and so on in the primary structure.

![Figure 1. Representative structures of high performance polymers](image-url)
Most of high performance polymers have been prepared by the polycondensation because the applicable monomers to prepare them could be widely as mentioned above. High performance polymers exhibit not only excellent thermal stability and mechanical properties but also chemical resistance, weather resistance, dimensional stability and abrasive resistance. Well known properties as an indicator of high performance polymers are $150^\circ \text{C} \geq$ deformation temperature, tensile strength $\geq 49 \text{ MPa}$ and bending modulus $\geq 2.4 \text{ GPa}$. Recently, these materials are currently receiving considerable attention for the applications in aerospace, automobile, electronics, and other technology fields as alternative materials of metal in industrial fields. [27, 28]

However, as with commodity polymers, most of high performance polymers also have been prepared from petroleum-based aromatic monomers. From the viewpoint of the suppression of the petroleum consumption to establish the sustainable development society, it is of great importance to replace the monomers from the petroleum-based materials to the biomass-based materials which are renewable resources. Many studies have focused on the introduction of bio-based moiety into main chain of polymer. [29-49] Nevertheless, few investigations have been reported on the bio-based high performance polymers because the bio-based monomers which can be raw materials for high performance polymers were limited.

Among many bio-based monomers, 2,5-furandicaboxlyc acid (FDCA) is efficiently prepared from cellulose, glucose and fructose as illustrated in Figure 2 by bio-refinery and is converted into other compounds easily. [29, 50-56] In fact, FCDA was selected as
one of the bio-based 12 key compounds as shown in Figure 3 by national research institution in USA. [54] FDCA has been attracted attention as a bio-based dicarboxylic acid comparable or substitutable to commercially available terephthalic acid, isophthalic acid and 2,6-naphthalenedicarboxylic acid. A plenty of types of polyesters, polyamides and others have been synthesized from FDCA and its related compounds by polycondensation, and investigated mainly on the thermal properties from 1960s. [29, 57-92] Table 1 shows the representative structures and properties of furan-ring polymers. For example, it has been reported that poly(ethylene 2,5-furandicarboxylate) synthesized from FDCA exhibited good thermal properties comparable to the homologue poly (ethylene terephthalate). [57, 58] Aromatic polyamides have been synthesized from FDCA and aromatic diamine such as \( p \)-phenylenediamine, 4,4’-oxydianiline and bis(4-aminophenyl)sulfone. [59-61] The polyamide prepared from

![Cellulose to Glucose](image1)

![Fructose to Furfural](image2)

![2,5-Furandicarboxylic acid (FDCA)](image3)

**Figure 2.** Preparation of FDCA from cellulose and fructose
FDCC and $p$-phenylenediamine exhibited lyotropic liquid-crystallinity in $N$-methylpyrrolidone. [59] It is conceivable that FDCA possesses enough potential for monomers of high performance polymers. However, few systematic investigations have been reported about preparation of high performance polymers so far. Furthermore, the detailed properties of furan-ring containing polymers have not been clarified. Therefore, it is necessary to grasp a potential for high performance polymers of furan-ring containing polymers.

Figure 3. Bio-based 12 key compounds reported by national research institution in USA
Table 1 The previously synthesized representative polymers derived from furan-based monomers

<table>
<thead>
<tr>
<th>Structure</th>
<th>$T_m^{a}^{\circ}C$</th>
<th>$T_g^{b}^{\circ}C$</th>
<th>Note</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>[OH$_2$C(\overbrace{\text{\begin{array}{c}^\begin{array}{c}O \end{array}}\end{array}})(\overbrace{\text{\begin{array}{c}O \end{array}}})_n]</td>
<td>No data</td>
<td>No data</td>
<td>Molecular weight was low (DP$_n$$\leq$5).</td>
<td>61</td>
</tr>
<tr>
<td>[OH$_2$C(\overbrace{\text{\begin{array}{c}O \end{array}})(\overbrace{\text{\begin{array}{c}O \end{array}})((\overbrace{\text{\begin{array}{c}\text{CH}_2\text{CH}_2\text{O} \end{array}}))_n]</td>
<td>180</td>
<td>45</td>
<td>Stable up to 280$^\circ$C</td>
<td>61</td>
</tr>
<tr>
<td>[(\overbrace{\text{\begin{array}{c}\text{CH}_2\text{CH}_2\text{O} \end{array}}))_n]</td>
<td>No data</td>
<td>No data</td>
<td>Stable up to 250$^\circ$C</td>
<td>62</td>
</tr>
<tr>
<td>[(\overbrace{\text{\begin{array}{c}\text{CH}_2\text{CH}_2\text{O} \end{array}}))_n]</td>
<td>No data</td>
<td>No data</td>
<td>Molecular weight was very low.</td>
<td>62</td>
</tr>
<tr>
<td>[(\overbrace{\text{\begin{array}{c}\text{CH}_2\text{CH}_2\text{O} \end{array}}))_n]</td>
<td>No data</td>
<td>191-196</td>
<td>Low crystallinity, Stable up to 320$^\circ$C</td>
<td>64</td>
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<tr>
<td>[(\overbrace{\text{\begin{array}{c}\text{CH}_2\text{CH}_2\text{O} \end{array}}))_n]</td>
<td>212</td>
<td>80</td>
<td>High crystallinity, Stable up to 300$^\circ$C,</td>
<td>57, 58</td>
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<tr>
<td>[(\overbrace{\text{\begin{array}{c}\text{CH}_2\text{CH}_2\text{O} \end{array}}))_n]</td>
<td>174</td>
<td>50</td>
<td>Stable up to 300$^\circ$C,</td>
<td>58</td>
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<tr>
<td>Structure</td>
<td>$T_m (^\circ C)$</td>
<td>$T_g (^\circ C)$</td>
<td>Note</td>
<td>Ref</td>
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<td>No data</td>
<td>Stable up to 250$^\circ$C</td>
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<tr>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>Depend on molar ratio of monomers</td>
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<td>Thermotropically liquid crystalline, Stable up to 400$^\circ$C</td>
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<td><img src="image3.png" alt="Structure 3" /></td>
<td>185</td>
<td>87</td>
<td>Stable up to 300$^\circ$C</td>
<td>57, 58</td>
</tr>
<tr>
<td><img src="image4.png" alt="Structure 4" /></td>
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<td>No data</td>
<td>High crystallinity, Stable up to 350$^\circ$C</td>
<td>58</td>
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<td><img src="image5.png" alt="Structure 5" /></td>
<td>225</td>
<td>320</td>
<td>Crystalline polymer</td>
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<td><img src="image6.png" alt="Structure 6" /></td>
<td>Decomposition</td>
<td>325</td>
<td>Lyotropically liquid crystalline, Stable up to 385$^\circ$C</td>
<td>59, 61</td>
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<td>Structure</td>
<td>$T_m (^\circ C)$</td>
<td>$T_g (^\circ C)$</td>
<td>Note</td>
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<td>Stable up to 315$^\circ$C</td>
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<td><img src="image3.png" alt="Structure 3" /></td>
<td>Decomposition</td>
<td>285</td>
<td>Stable up to 360$^\circ$C</td>
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<td>$T_g , (^{\circ}C)$</td>
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<tr>
<td>Structure</td>
<td>$T_m$ ($^\circ$C)</td>
<td>$T_g$ ($^\circ$C)</td>
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<td>No data</td>
<td>No data</td>
<td>61, 66</td>
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</table>

*a* Melting temperature  
*b* Glass transition temperature
AIM AND STRATEGY OF THIS THESIS

As the first trial to reduce the ratio of petroleum-based moiety in high performance polymers, the aims of this thesis are to synthesize aromatic polymers by the polycondensation of FDCA and petroleum-based compounds, and to examine their potentiality as high performance polymers by comparing their properties with common high performance polymers. It is conceivable that the polycondensations of FDCA and the related compounds can afford a variety of polymers such as polyesters (PEss), polyamides and poly(ether ketone)s (PEKs), and so on. As aforesaid, some of furan-ring containing polyesters and polyamides have been synthesized, and the properties became obvious little by little. However, PEKs and wholly aromatic PEss which are known as representative high performance polymers have been hardly synthesized by the polycondensation of FDCA and investigated on the detailed properties so far.

The strategy of this thesis is mapped out in the following in order to accomplish this study. At first, the polycondensation is adapted to prepare furan-ring containing aromatic poly(ether ketone)s (F-PEK). Common PEKs are well-known as high performance semicrystalline polymers possessing not only excellent chemical resistance, physical, and mechanical properties but also processability. [27, 28] The thermal properties such as glass transition temperature and melting temperature of them are tunable with the ratio of ketone and ether linkage. [93] A plenty of types of PEKs have been industrially synthesized with changing their sequence of ether groups and ketone
groups in the repeating units. Therefore, PEKs have been widely used as industrial materials, and they are currently receiving considerable attention for the applications in aerospace, automobile, electronics, and other technology fields. Preparations of PEKs are classified into two reactions. One is the aromatic electrophilic substitution polymerization, so-called Friedel–Crafts polymerization, between aromatic diacid chlorides and electron-rich aromatic hydrocarbons to form the ketone linkages. [94-99] The Friedel-Crafts polymerizations are generally carried out in organic solvents with a catalyst of aluminum chloride (AlCl₃) under moderate conditions. Hence, the Friedel–Crafts polymerization is more suitable to use FDCA as a monomer. Furthermore, the dehydrative acylation polymerizations were also reported in polyphosphoric acid, [100] in trifluoromethanesulfonic acid [101] and in a methanesulfonic acid/phosphorus pentoxide mixture. [102] In the dehydrative methods, usable monomers were generally limited: i.e. typical aromatic dicarboxylic acid such as terephthalic acid and isophthalic acid could not be used in this method. [102] Further, side reactions such as decarboxylation were occurred under high polymerization temperature. [102] Hence, the Friedel-Crafts polymerizations of 2,5-furandicarboxylic acid dichloride (FDCC) which is a diacid chloride of FDCA and the aromatic ethers in presence of Lewis acid as catalyst were adaptable to prepare F-PEKs. Another is the aromatic nucleophilic substitution polymerization between activated aromatic dihalides and alkali metal phenoxides to form the ether linkage. [103-105] This method is used for the production of not only commercially available poly(ether ether ketone) which is
a most popular PEKs in them but also commercial poly(ether sulfone)s. In general, aromatic dihalides are used for this procedure as monomers. Since aromatic dihalides can be prepared from FDCA, there is a possibility that F-PEKs are synthesized from aromatic dihalides and alkali metal phenoxides.

Next, the preparation of wholly aromatic PEss (F-PEss) is examined by the polymerization of FDCA and petroleum-based aromatic diacetates. Wholly aromatic PEss are industrially used as high performance engineering materials. [27, 28] In particular, thermotropic liquid-crystalline PEss possess excellent thermal stability, mechanical properties and processability. [27, 106] As mentioned above, wholly which aromatic PEss have been hardly synthesized by the polycondensation of FDCA and aromatic acetates. [89, 90] Although wholly aromatic PEs has been synthesized by the interfacial polymerization of FDCC and hydroquinone, it exhibit neither meltability nor solubility due to the rigid structure. [58] In general, since wholly aromatic PEss possess a potential to form thermotropic liquid-crystallinity phase, [107-111] F-PEss may exhibit thermotropic liquid-crystallinity.

Based on the above strategies, the preparation of aromatic F-PEKs and wholly aromatic F-PEss from FDCA and evaluation of their properties were investigated in this thesis. This thesis consists of three chapters. The Friedel-Crafts polymerization of FDCC and aromatic ethers such as diphenyl ether (DPE) and 1,4-diphenoxynbenzene (DPB) is investigated end in Chapter 1. The polymerizations are carried out in molecular solvents and ionic liquids. The unique polymerization behavior is discussed
in this chapter. In Chapter 2, the aromatic nucleophilic substitution polymerization of aromatic dihalide prepared from FDCA and aromatic bisphenoxides is investigated. The fundamental knowledge of the aromatic nucleophilic substitution polymerization of the furan-ring containing dihalide and physical properties of them are examined. In the last Chapter 3, the polymerizations of FDCA and diacetoxybenzene as aromatic diacetates by transesterification are carried out to obtain F-PEss. Further, the F-PEss were characterized with the comparison of PEss prepared from terephthalic acid, isophthalic acid and 2,5-thiophenedicarboxylic acid.

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CHAPTER 1

PREPARATION OF AROMATIC POLY(ETHER KETONE)S BY
FRIEDEL-CRAFTS POLYCONDENSATION

1-1 Preparation of Poly(ether ketone)s Containing Furan-Ring

1-1-1 Introduction

Aromatic PEKs are well known as high performance semicrystalline polymers possessing not only excellent chemical, physical, and mechanical properties but also processability. [1, 2] They also possess good chemical resistance because of inert against common organic solvents. [1] The properties such as glass transition temperature and melting temperature of them are tunable with the ratio of ketone and ether linkage. [3, 4] Commercially available poly(ether ether ketone) so-called VICTREX® which is representative aromatic PEKs have been widely used as industrial materials, and they are currently receiving considerable attention for the applications in aerospace, automobile, electronics, and other technology fields nowadays. However, as aforesaid, PEKs have been prepared from petroleum-based aromatic monomers such as terephthalic acid and isophthalic acid. From the viewpoint of the suppression of the petroleum consumption to establish the sustainable development society, it is of great
importance to replace the monomers from the petroleum-based materials to the biomass-based materials. Although, bio-based aliphatic-aromatic PEKs have been synthesized from 1,4:3,6-dianhydrohexitol such as isosorbide, isomannide and isoidide, and 4,4’-difluorobenzophenone, [5] wholly aromatic PEKs have not been synthesized from bio-based monomers so far. As described above, The Friedel–Crafts polymerization is one of the preparation method of PEKs. The Friedel–Crafts polymerizations were carried out between aromatic diacid chlorides and electron-rich aromatic hydrocarbons to form the ketone linkages. [6-12] Furthermore, the dehydrative acylation polymerizations were also reported in polyphosphoric acid, [13] in trifluoromethanesulfonic acid [14] and in a methanesulfonic acid/phosphorus pentoxide mixture. [15] In the dehydrative methods, usable monomers were limited and side reactions such as decarboxylation were occurred under high polymerization temperature. [15] Hence, the Friedel–Crafts polymerization of FDCC which is a diacid chloride of FDCA and electron-rich aromatic hydrocarbons is more suitable to prepare F-PEKs.

In this Chapter, as the first trial to reduce the ratio of petroleum-based moiety in aromatic PEKs, this work aims to synthesize PEKs (F-PEKs) from FDCC and petroleum-based aromatic ethers such as diphenyl ether (DPE), and 1,4-diphenoxybenzene (DPB) by the Friedel-Crafts polymerization as illustrated in Scheme 1-1 and to characterize them with the comparison of common PEKs.
FDCA (TCI Co. Ltd.) was purified by recrystallization from water. Terephthalic and isophthalic acid (Sigma Aldrich Co. Ltd.) were purified by the sublimation. DPE (Nacalai Tesque Co. Ltd.) and nitrobenzene (NB, Tokyo Kasei Kogyo Co. Ltd.) were purified by vacuum distillation. DPB (TCI Co. Ltd.) was purified by recrystallization from ethanol. 1,2-Dichloroethane (DCE; TCI Co. Ltd.) was distilled over calcium hydrate. 1-\textit{n}-Alkyl-3-methylimidazolium chloride ([C\textit{n}mim]Cl; TCI Co. Ltd.), 1-\textit{n}-alkyl-3-methylimidazolium iodide ([C\textit{n}mim]I; Sigma Aldrich Co. Ltd.) and 1-\textit{n}-alkyl-3-methylimidazolium trifluoromethanesulfonate ([C\textit{n}mim]OTf; Sigma Aldrich Co. Ltd.) were dehydrated at 100\textdegree C for 12 h under 0.3 mmHg prior to use. AlCl\textsubscript{3} (TCI Co. Ltd.), Zinc(+II) Chloride (ZnCl\textsubscript{2}; Wako Co. Ltd.), Tin(+IV) Chloride
(SnCl₄; Sigma Aldrich Co. Ltd.), N,N-dimethylformamide (DMF; Sigma Aldrich Co. Ltd.), N,N-dimethylacetamide (DMAc; Sigma Aldrich Co. Ltd.), N-methylpyrrolidone (NMP; Sigma Aldrich Co. Ltd.), dimethyl sulfoxide (DMSO; Sigma Aldrich Co. Ltd.), 97% sulfuric acid (Nacalai Tesque Co. Ltd.), trifluoroacetic acid (TFA; TCI Co. Ltd.), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP; TCI Co. Ltd.) and 2,3,4,5,6-pentafluorophenol (5FPhOH; TCI Co. Ltd.) were used as received.

1-1-2-2 Synthesis of Diacid Chloride

FDCC was synthesized from FDCA and thionyl chloride by the previously reported procedure. [16] Obtained FDCC was purified by recrystallization from n-hexane, and following sublimation under 0.2 mmHg. Terephthaloyl chloride (TPC) and isopthaloyl chloride (IPC) were also prepared from terephthalic and isophthalic acid by the same manner.

1-1-2-3 Polymerization

1-1-2-3-1 Polymerization in Molecular Solvents

In a 25 mL of three-necked flask equipped with a nitrogen inlet and a stirrer, aromatic ether (2.4 mmol) and FDCC (0.47 g, 2.4 mmol) were dissolved in DCE or NB (10 mL). The reaction mixture was allowed to cool at -10°C, and AlCl₃ (1.35 g, 10.1 mmol) was
added to the mixture under stirring. In this case, the molar ratio of AlCl₃ to FDCC in feed (\(f_3\)) was 4.2. Then the mixture was stirred at \(-10^\circ\text{C}\) for 1 h and heated up to \(20^\circ\text{C}\) for 0.5 h under dry nitrogen. The polymerization was continued at \(20^\circ\text{C}\) for 20-120 h. The mixture was poured into methanol. The precipitates were isolated by filtration and washed with methanol using a Soxhlet extractor for 24 h.

1-1-2-3-2 Polymerization in Ionic Liquids

The polymerization in \([\text{C}_4\text{mim}]\text{Cl}\) was described as typical procedure. Dehydrated \([\text{C}_4\text{mim}]\text{Cl}\) (10.0 g, 57.2 mmol) and AlCl₃ (19.7 g, 148 mmol) were mixed at \(20^\circ\text{C}\) for 12 h. Aromatic ether (2.4 mmol), FDCC (0.47 g, 2.4 mmol) and ionic liquid-AlCl₃ mixture (10 mL, 13.1 g) were placed into a 25 mL three-necked flask equipped with a nitrogen inlet and a stirrer, and then the mixture was stirred for 10 min at \(25^\circ\text{C}\) under dry nitrogen. The polymerization was performed at a given temperature for 24 h. Polymers were collected by the same manner as mentioned above.

1-1-2-4 Measurements and Characterization

Fourier transform infrared (FT-IR) spectra were measured on a FT/IR-410 spectrometer (JASCO Co. Ltd.). Wide angle X-ray scattering (WAXS) patterns were measured on a Gaiger Flex (Rigaku Co. Ltd.) with nickel-filtered Cu-K\(\alpha\) radiation (35
kV, 15 mA). Thermal properties were measured on a Perkin–Elmer TGA-7 (Perkin Elmer Cetus Instruments) at a heating rate of 10°C/min under a nitrogen flow of 20 mL/min. Glass-transition temperature \( T_g \) and melting temperature \( T_m \) were measured on a DSC-8000 (Perkin Elmer Cetus Instruments) at a scanning rate of 10°C/min in nitrogen atmosphere. Reduced viscosities \( \eta_{sp}/c \) were measured with an Ostwald type viscometer at a concentration of 0.1 g/dL in 97% sulfuric acid at 25°C. 300 MHz \(^1\)H-NMR spectra were obtained on a Varian Unity-500 spectrometer in a mixture of CDCl\(_3\) and TFA. Matrix assisted laser desorption ionization time-of-flight mass (MALDI-TOF MS) spectrometry was performed on a Bruker Daltonics AutoFLEX MALDI-TOF MS system operating with a 337 nm N\(_2\) laser. Spectra were obtained in the linear positive mode with an accelerating potential of 20 kV. Mass calibration was performed with angiotensin I (MW 1296.69) and insulin B (MW 3496.96) from a Sequazyme peptide mass standard kit. Samples were then prepared by the evaporation-grinding method and ran in 1,8-dihydroxy-9(10H)-anthracenone as a matrix doped with potassium trifluoroacetate. A solubility test was carried out at 0.05 g/dL in several solvents at 25°C.

1-1-2-5 Measurement of Kinetic Parameters of Model Reaction

Reaction kinetics was measured by acid-base titration. FDCC (0.40g, 2.08 mmol), anisole (0.45 g, 4.16 mmol) and the solvents (10 mL) were placed into a 25 mL of
three-necked flask equipped with nitrogen inlet and outlet tubes, and a stirrer. AlCl₃ was added to the mixture, and the mixture was stirred at a predefined temperature under a stream of dry nitrogen. Hydrochloric gas which was a by-product was trapped in the water and titrated with 0.1 mol L⁻¹ sodium hydroxide solution with the compensation of the amount of generated hydrogen chloride by hydrolysis of AlCl₃.

1-1-2-6 Evaluation of Degree of Swelling of Precipitate

Degree of swelling of the precipitate (Dₛ) was described as the weight ratio of dried precipitates to as polymerized precipitates.

1-1-3 Results and Discussion

1-1-3-1 Polymerizations in Molecular Solvents

In general, the Friedel-Crafts polymerization is carried out in chlorinated hydrocarbons such as DCE with excess AlCl₃ to diacid chlorides because of formation of 1:1 complex of carbonyl group of acid chloride and AlCl₃. [17, 18] When TPC and IPC were used as diacid chlorides, the optimum fₓ was reported to be 2.7-2.9. [10-12] In the polymerization, AlCl₃ was added to the monomer solution below 0°C. Thereafter, the polymerization temperature was raised to 20°C and the polymerization was performed at 20°C for ca. 20 h. It had been revealed that the physical gel of the oligomer-AlCl₃
complex was formed at the early stage of polymerization, and then polymerization underwent in the physical gels swollen by DCE. [17] Furthermore, the molecular weight of PEKs generally depends on the polymerization concentration. [11] In this study, according to the previous results, the polymerizations of FDCC and DPE or DPB were carried out in DCE with changing polymerization concentration. PEK prepared from FDCC and DPE was described as F-PEK(DPE), and that from FDCC and DPB was done as F-PEK(DPB). After the polymerization, the polymerization was terminated by methanol, and the products extracted by hot methanol to remove residual deactivated catalyst and low molecular weight oligomers. Precipitation occurred in the solution rapidly after the addition of AlCl₃. Table 1-1 summarized the results of polymerization. Results of the polymerization of TPC or IPC and DPE in DCE are also presented in Table 1-1 for the comparison. The PEK prepared from TPC and DPE was described as T-PEK(DPE), and that from IPC and DPE was done as I-PEK(DPE). The yields and the reduced viscosities of the F-PEKs were considerably lower than T-PEK(DPE) and I-PEK(DPE) at $f_c$ of 2.8 in any concentrations. Since it was conceivable that the AlCl₃ might be deactivated due to the coordination of ether group in furan-ring to AlCl₃, the polymerizations were carried out at $f_c$ of 3.6 and 4.2. However, these values were still low. Although C=O stretching peak of ketone group and C-O-C stretching peak of ether group were observed at 1641 cm⁻¹ and 1250 cm⁻¹, C=O and C-O-C stretching peaks of ester group were observed clearly which was formed during termination by the reaction of acid chloride and methanol as shown in Figure 1-1. These results and the low values
Table 1-1. Polymerization results of F-, T-, and I-PEK(DPE) and F-PEK(DPB) in molecular solvents

<table>
<thead>
<tr>
<th>Polymer code</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>$f_c^b$</th>
<th>Conc. $^c$</th>
<th>Yield (%)</th>
<th>$\eta_{sp/c}^d$ (dL/g)</th>
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</thead>
<tbody>
<tr>
<td>F-PEK(DPE)</td>
<td>AlCl$_3$</td>
<td>DCE</td>
<td>2.8</td>
<td>3</td>
<td>1</td>
<td>- $^e$</td>
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<tr>
<td>F-PEK(DPE)</td>
<td>AlCl$_3$</td>
<td>DCE</td>
<td>2.8</td>
<td>6</td>
<td>24</td>
<td>0.05</td>
</tr>
<tr>
<td>F-PEK(DPE)</td>
<td>AlCl$_3$</td>
<td>DCE</td>
<td>2.8</td>
<td>9</td>
<td>25</td>
<td>0.05</td>
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<tr>
<td>F-PEK(DPE)</td>
<td>AlCl$_3$</td>
<td>DCE</td>
<td>3.6</td>
<td>6</td>
<td>20</td>
<td>0.02</td>
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<td>AlCl$_3$</td>
<td>DCE</td>
<td>4.2</td>
<td>7</td>
<td>25</td>
<td>0.05</td>
</tr>
<tr>
<td>F-PEK(DPE)</td>
<td>ZnCl$_2$</td>
<td>DCE</td>
<td>4.2</td>
<td>7</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>F-PEK(DPE)</td>
<td>SnCl$_4$</td>
<td>DCE</td>
<td>4.2</td>
<td>7</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
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<td>AlCl$_3$</td>
<td>NB</td>
<td>4.2</td>
<td>6</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>T-PEK(DPE)</td>
<td>AlCl$_3$</td>
<td>DCE</td>
<td>2.8</td>
<td>3</td>
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<td>I-PEK(DPE)</td>
<td>AlCl$_3$</td>
<td>DCE</td>
<td>2.8</td>
<td>10</td>
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<td>0.98</td>
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<tr>
<td>F-PEK(DPB)</td>
<td>AlCl$_3$</td>
<td>DCE</td>
<td>2.8</td>
<td>6</td>
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<td>F-PEK(DPB)</td>
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<td>4.2</td>
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<tr>
<td>F-PEK(DPB)</td>
<td>AlCl$_3$</td>
<td>NB</td>
<td>4.2</td>
<td>6</td>
<td>2</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Polymerizations were carried out at a temperature of 20°C for 20 h. $^b$ Molar ratio of AlCl$_3$ to diacid chlorides in feed. $^c$ Ratio of weight of polymer at the extent of reaction of 1.0 and volume of solvents. $^d$ Reduced viscosities were measured in 97% H$_2$SO$_4$ at a concentration of 0.1 g/dL and 25°C. $^e$ Impossible to measure due to the low yield
of the reduced viscosity revealed that low molecular weight F-PEKs were formed in DCE. It was reported that the oxyphilicity of Lewis acid increased in following order: SnCl₄ < ZnCl₂ < TiCl₄ < AlCl₃. [18] Since it was conceivable that the polymerizations with low oxyphilicity catalysts such as SnCl₄ and ZnCl₂ might proceed due to the suppression of the coordination of ether group in furan-ring to catalyst, the

**Figure 1-1.** FT-IR spectra of (a) F-PEK(DPE) and (b) F-PEK(DPB) prepared by AlCl₃ in DCE for 20 h, and (c, d) the reaction mixture which were recovered from the reaction solution and prepared by ZnCl₂ and SnCl₄, respectively.
polymerizations of FDCC and DPE were carried out at \( f_c \) of 4.2 with these catalysts in DCE. However, the polymerizations did not proceed at all. The reaction mixtures recovered from the reaction solution were analyzed by FT-IR as shown in Figure 1-1 (c, d). The C=O stretching peak of ketone group was not observed at all, and C=O and C-O-C stretching peaks of ester group were observed clearly. The mixtures were analyzed by \(^1\)H-NMR spectrum of the reaction mixture prepared by SnCl\(_4\) was illustrated in Figure 1-2. The spectrum was exactly the same as 2,5-dimethylfurandicarboxylate which was formed during termination by the reaction of FDCC and methanol, and DPE. It is known that the cyclic oligomers are often formed in polycondensation system of polyesters, polyamides, poly(ether sulfone)s and so on. [19] The oligomers recovered from the reaction solution were analyzed by MALDI-TOF mass. The spectrum of oligomers from FDCC and DPE, and the peak

\[ \text{Figure 1-2. } ^1\text{H-NMR spectrum of the reaction mixture prepared by SnCl}_4 \text{ in DMSO-}d_6 \text{ after removal of SnCl}_4 \text{ and solvent} \]
assignments were presented in Figure 1-3 and Table 1-2, respectively. The peaks attributed to the cyclic oligomer were not detected. The longer time might be needed to increase molecular weight of F-PEKs than that of the common Friedel-Crafts polymerization due to the lower reactivity of acylium ion of \( \pi \)-electron rich of furan ring. Therefore, the polymerization was next carried out for the longer time. Figure 1-4 plotted the yield and the reduced viscosity of F-PEK(DPE) at a concentration of 7% at \( f_c \) of 4.2 as a function of time. Although, the yields and the reduced viscosities increased proportionally with time, the yield was only 70% after 120 h at most. Furthermore, F-PEK(DPE) turned out to be partially insoluble in sulfuric acid after 72 h. It had been reported that cross-linking reaction occurred at high reaction temperature [20] but various side reactions occurred even at low reaction temperature. [21] The side reaction might

![Figure 1-3. MALDI-TOF MS spectrum of the oligomer prepared from FDCC and DPE in DCE at a concentration of 7% and \( f_c \) of 4.2](image-url)
occur after 72 h bringing about the formation of some nonlinear defect structure. In addition, the polymerization in NB which was a common solvent for organic synthesis by the Friedel-Crafts reaction did not yield the product and the polymerization hardly proceeded.

<table>
<thead>
<tr>
<th>Peak code</th>
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<th>n</th>
<th>Mass (m/z)</th>
</tr>
</thead>
<tbody>
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<td>323.32 322.68</td>
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<tr>
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<td>B&lt;sub&gt;n&lt;/sub&gt;</td>
<td>1</td>
<td>361.14 360.67</td>
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<td>2</td>
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<td>941.96 940.79</td>
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<td>675.75 674.70</td>
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<td>498.51 498.78</td>
</tr>
</tbody>
</table>
As mentioned above, the Friedel-Crafts polymerization usually proceeds in adequately swollen gel of oligomer-AlCl$_3$ complex. Therefore, it is of great importance to carry out the polymerization in the suitable solvents which possess high affinity to the oligomer-catalyst complexes. The polymerization of FDCC and the aromatic ethers hardly proceeded in DCE because the oligomers-AlCl$_3$ complexes were immiscible to the DCE, and the precipitates were not enough swollen to polymerize. The affinity of the oligomer and the solvent should be improved in order to prepare high molecular

Figure 1-4. Polymerization time dependencies of yield (●) and reduced viscosity (○) of F-PEK(DPE) at a concentration of 7% and χ of 4.2 in DCE

1-1-3-2 Polymerizations in Ionic Liquids

As mentioned above, the Friedel-Crafts polymerization usually proceeds in adequately swollen gel of oligomer-AlCl$_3$ complex. Therefore, it is of great importance to carry out the polymerization in the suitable solvents which possess high affinity to the oligomer-catalyst complexes. The polymerization of FDCC and the aromatic ethers hardly proceeded in DCE because the oligomers-AlCl$_3$ complexes were immiscible to the DCE, and the precipitates were not enough swollen to polymerize. The affinity of the oligomer and the solvent should be improved in order to prepare high molecular
weight F-PEKs. It was reported that ionic liquids such as \([C_n\text{mim}]\text{Cl}-\text{AlCl}_3\) and \([C_n\text{mim}]\text{I}-\text{AlCl}_3\) mixture worked as the solvent and catalyst of the Friedel-Crafts reactions. [22-25] Ionic liquids such as \([C_4\text{mim}]\text{Cl}\) have been paid attention as next-generation solvent due to their unique properties. Specific ionic liquids can be dissolved polysaccharides such as cellulose. [26] These facts can be expected that the ionic liquid would swell the oligomer-AlCl_3 complexes due to higher affinity to afford higher molecular weight F-PEKs. Based on this, the polymerizations were carried out in ionic liquids of \([C_n\text{mim}]\text{Cl}, [C_n\text{mim}]\text{I} \text{ and } [C_n\text{mim}]\text{OTf} \) with changing the molar ratio of AlCl_3 to ionic liquids, polymerization time and temperature. Figure 1-5, 1-6 and 1-7 summarized the results of the polymerizations. The polymerizations proceeded well in \([C_4\text{mim}]\text{Cl}-\text{AlCl}_3\) mixture and the reduced viscosities of F-PEK(DPE) and F-PEK(DPB) were higher than that in DCE at a concentration of 7-10% and 60°C for 24 h. In contrast, the polymerizations did not proceed in \([C_n\text{mim}]\text{I} \text{ and } [C_n\text{mim}]\text{OTf}\), and also did not proceed at lower temperature in \([C_4\text{mim}]\text{Cl}\). Moreover, the polymerization proceeded in presence of AlCl_3 more than twice equimolar to ionic liquids as shown in Figure 1-8. The influence of polymerization temperature and the molar ratio of AlCl_3 to ionic liquids are discussed later. Although C=O stretching peak of ester was slightly observed at 1723 cm\(^{-1}\), C=O stretching peak of ketone group was clearly detected at 1644 cm\(^{-1}\) in the spectrum of F-PEK(DPE) as presented in Figure 1-9. These results revealed that the ionic liquid \([C_4\text{mim}]\text{Cl}\) worked as a polymerization medium. The reusability of ionic liquids for the polymerization was of importance especially for the industrially and
Figure 1-5. Influence of structure of ionic liquid on yield and reduced viscosity of F-PEK(DPE) at a conc. of 7% and the ratio of AlCl₃ to ionic liquids of 2.6 for 24h: [C₄mim]Cl (◆, ◇), [C₄mim]Cl (■, □), [C₈mim]Cl (●, ○), [C₂mim]I (▼, ▽), [C₄mim]I (▲, ▼), and [C₄mim]OTf (▲, △)
Solid marks : Yield, Open marks : Reduced viscosity

Figure 1-6. Plots of yield and reduced viscosity of F-PEK(DPE) as a function of polymerization time at a conc. of 7% and the ratio of AlCl₃ to ionic liquids of 2.6 in [C₄mim]Cl: 60°C (●, ○) and 50°C (▲, △)
Solid marks : Yield, Open marks : Reduced viscosity
Figure 1-7. Plots of yield and reduced viscosity of F-PEKs as a function of concentration at the ratio of AlCl₃ to ionic liquids of 2.6 for 24h in [C₄mim]Cl: F-PEK(DPE) (●, ○) and F-PEK(DPB) (◆, ◇)
Solid marks : Yield, Open marks : Reduced viscosity

Figure 1-8. The molar ratio ([AlCl₃]/[[C₄mim]Cl]) dependencies of yield and reduced viscosity of F-PEK(DPE) (●, ○) and F-PEK(DPB) (◆, ◇) at a conc. of 7% for 24h: Solid marks: Yield, Open marks : Reduced viscosity
environmental aspects. Based on this, the polymerization of FDCC and DPE in recycled $[\text{C}_4\text{mim}]\text{Cl}$ was examined to confirm the reusability of ionic liquids. After the polymerization, methanol was added to $[\text{C}_4\text{mim}]\text{Cl}-\text{AlCl}_3$ mixture to deactivate. Methanol was evaporated, and oligomers left in the mixture were subsequently removed by washing with acetone several times. Then, $[\text{C}_4\text{mim}]\text{Cl}$ was extracted by ethyl acetate. Ethyl acetate was evaporated and the $[\text{C}_4\text{mim}]\text{Cl}$ was dried at 100°C under vacuum for 12 h. The obtained $[\text{C}_4\text{mim}]\text{Cl}$ was used for the polymerization of FDCC and DPE. Although the yield and reduced viscosity of F-PEK(DPE) prepared in recycled $[\text{C}_4\text{mim}]\text{Cl}$ were 94% and 0.25 dL/g, respectively, which were slightly lower than those of 99% and 0.31 dL/g of the F-PEK(DPE) prepared in virgin $[\text{C}_4\text{mim}]\text{Cl}$ under the same condition, $[\text{C}_4\text{mim}]\text{Cl}$ could be reusable for the preparation of F-PEK by Friedel-Crafts
polycondensation. $^1$H-NMR spectra of F-PEKs are illustrated in Figure 1-10. The spectra show a singlet at about 7.5 ppm for the furan ring protons, multiplet in the range of 7.05 to 7.25 ppm and that of 8.0 to 8.2 ppm for phenyl protons. The number average molecular weight ($M_n$) of F-PEK(DPE) and F-PEK(DPB) were $7.2 \times 10^3$ and $1.3 \times 10^4$ respectively, calculated from end-group analysis by $^1$H-NMR. They contained para-isomer to ether-linkage with the small amount of ortho-isomer because DPE and DPB have several reaction points which are the electron rich para- and ortho-position carbons to ether-linkage. In this case, DPE has reactive carbons at the 2 para- and 4 ortho-position, and DPB does reactive carbons at 2 para- and 8 ortho-position carbons. The amount of ortho-isomer were approximately 5% for F-PEK(DPE) and 11% for F-PEK(DPB). The polymerizations did not also proceed in $[C_4\text{mim}]\text{Cl}-\text{ZnCl}_2$ and $[C_4\text{mim}]\text{Cl}-\text{SnCl}_4$ mixtures because these catalysts were not mixed with $[C_4\text{mim}]\text{Cl}$ at all as discussed later.
Figure 1-10. $^1$H-NMR spectra of (a) F-PEK(DPE) and (b) F-PEK(DPB) measured in CDCl$_3$/CF$_3$CO$_2$H
1-1-3-3 Polymerization Behavior

The polymerization of FDCC and aromatic ethers in ionic liquids, especially [C₄mim]Cl afforded high molecular weight F-PEKs, but that in DCE did not yield F-PEKs. The solvent effect on the polymerization behavior is very interesting. The Friedel-Crafts polymerization proceeds in heterogeneous phase with the formation of gels as described above. Based on this unique polymerization behavior, it is conceivable that the reactivity of monomers and the affinity of the oligomers-catalyst complex in the solvents influence the polymerization behavior significantly. The polymerization behavior was examined from the viewpoint of the swelling behavior of precipitates and the kinetics of model reaction to clarify the specific polymerization in ionic liquids.

1-1-3-3-1 Swelling Behavior

Figure 1-11 was the plot of the $D_s$ values as a function of time for the polymerization of FDCC and DPE in various solvents. As for the polymerizations in NB, the precipitations did not occur. Precipitation occurred rapidly in DCE after the addition of AlCl₃. The $D_s$ was about 55% at 1 h and decreased drastically with time until 20 h, and then leveled off to ca. 30%. It has been previously reported that the precipitates formed in the polymerization of IPC and DPE in DCE maintained high $D_s$ of ca. 55% even after the middle stage of polymerization. [17] These results indicate that the precipitates
formed in the polymerization of FDCC and the aromatic ethers were not enough swollen by DCE due to the low affinity between the solvent and oligomer-AlCl₃ complex. On the other hand, the precipitates did not occur in ionic liquids at the early stage of the polymerization, and the solution became gradually viscous with time. The solution in ionic liquids turned out to be jelly-like at 10 h. The $D_s$ in [C₄mim]Cl was about 57% at 12 h and decreased gradually with time. The $D_s$ of the precipitates formed in [C₂mim]Cl, [C₄mim]Cl and [C₈mim]Cl was about 50% at 24 h. Unlike DCE, the precipitates in [C₄mim]Cl were retained highly swollen after the middle stage of the polymerization. Among the ionic liquids, the precipitated gel formed in [C₄mim]Cl was

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**Figure 1-11.** Polymerization time dependencies of $D_s$ values of F-PEK(DPE) precipitates in DCE and ionic liquids: DCE (●), [C₂mim]Cl (×), [C₄mim]Cl (■), [C₈mim]Cl (○), [C₄mim]I (□), and [C₄mim]OTf (▲).
more highly swollen. The $D_s$ in [C$_4$mim]I and [C$_4$mim]OTf at 24 h were 45 and 43% respectively, and they were lower than that of [C$_4$mim]Cl. The structure of the as polymerized precipitates was examined by WAXS. Figure 1-12 shows the WAXS intensity profiles of the precipitates of F-PEK(DPE) prepared in DCE, [C$_4$mim]Cl and [C$_4$mim]OTf. The characteristic peaks were clearly detected attributed to the unit cell of
AlCl$_3$ in the profile of the precipitates in DCE. On the other hand, characteristic diffraction peaks were not observed in the profile of the gels precipitated in [C$_4$ mim]Cl and the precipitates did not have short range order structure. Unlike the precipitates in [C$_4$ mim]Cl, some diffraction peaks of that in [C$_4$ mim]OTf were clearly detected. This fact indicated that the precipitates were not enough swollen in [C$_4$ mim]OTf. According to these results, the swollen gels of the oligomer-AlCl$_3$ were efficiently formed in [C$_4$ mim]Cl.

1-1-3-3-2 Kinetics of Model Reaction

The model reaction of FDCC and anisole was followed by the titration of evolved hydrogen chloride with aqueous sodium hydroxide. The amount of hydrogen chloride generated by hydrolysis of AlCl$_3$ was compensated. Figure 1-13 showed the plot of the second-order kinetic reaction at the initial stage of the reaction. The model reactions at the early stage obeyed the second order kinetics in all solvents. Rate constants ($k_2$) and activation energies ($E_a$) were estimated as presented in Table 1-3. The values of $k_2$ at 60°C in DCE, NB and [C$_4$ mim]Cl were 4.9×10$^{-2}$, 2.3×10$^{-2}$ and 8.5×10$^{-2}$ L mol$^{-1}$ min$^{-1}$, respectively. Hence, the rate constant in [C$_4$ mim]Cl was 1.7 times higher than that in DCE at 60°C and the reactivity was enhanced in [C$_4$ mim]Cl. Although NB which is often used for organic synthesis by the Friedel-Crafts reaction, the $k_2$ was the lowest among solvents used in this work. NB is a Lewis base, deactivates AlCl$_3$ due to
coordination of NB to AlCl\textsubscript{3}. [18] In term of reactivity, NB is not suitable to the polymerization. \(E_a\) in [C\textsubscript{4}mim]Cl was 1.3 to 1.8 times higher than that in DCE and NB. It means that the reactivity in [C\textsubscript{4}mim]Cl depends strongly on the reaction temperature. In fact, the polymerizations in ionic liquids did not proceed well at lower reaction temperature as 50°C. High value of \(E_a\) in [C\textsubscript{4}mim]Cl is consistent with the results of polymerization. With respect to the structure of ionic liquid, the polymerizations of FDCC and the aromatic ethers proceeded well in [C\textsubscript{4}mim]Cl-AlCl\textsubscript{3} mixture. Furthermore, the \(k_2\) value of the model reaction and the \(D_s\) value in [C\textsubscript{4}mim]Cl were the highest among the ionic...
liquids. Ionic liquids are comprised of cation and anion parts. The nature of ionic liquids is drastically changed by the ion pairs. For instance, the dielectric constants of \([\text{C}_{2}\text{mim}]\text{Cl}\), \([\text{C}_{4}\text{mim}]\text{Cl}\) and \([\text{C}_{8}\text{mim}]\text{Cl}\) are about 12.0, 15.0 and 8.0, respectively. \([27, 28]\)

As for the cation, the reduced viscosities of F-PEKs prepared in ionic liquids were positively correlated with the dielectric constants of them. It was reported that the Friedel-Crafts reactions in \([\text{C}_{n}\text{mim}]\text{Cl}\) proceeded in presence of AlCl\(_3\) more than twice equimolar to ionic liquids to form chloroaluminate anion as activated species as

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>(k_2) (^b) (L mol(^{-1}) min(^{-1}))</th>
<th>(E_a) (^c) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCE</td>
<td>10</td>
<td>4.1×10(^{-3})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>9.8×10(^{-3})</td>
<td>38</td>
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<tr>
<td></td>
<td>30</td>
<td>1.2×10(^{-2})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>4.9×10(^{-2})</td>
<td></td>
</tr>
<tr>
<td>NB</td>
<td>5</td>
<td>3.0×10(^{-3})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>5.7×10(^{-3})</td>
<td>28</td>
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<td></td>
<td>40</td>
<td>1.3×10(^{-2})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>2.3×10(^{-2})</td>
<td></td>
</tr>
<tr>
<td>([\text{C}_{4}\text{mim}]\text{Cl})</td>
<td>40</td>
<td>2.2×10(^{-2})</td>
<td></td>
</tr>
<tr>
<td>([\text{C}_{4}\text{mim}]\text{OTf})</td>
<td>60</td>
<td>1.9×10(^{-2})</td>
<td>-</td>
</tr>
<tr>
<td>([\text{C}_{4}\text{mim}]\text{I})</td>
<td>60</td>
<td>4.2×10(^{-3})</td>
<td>-</td>
</tr>
<tr>
<td>([\text{C}_{4}\text{mim}]\text{I})</td>
<td>60</td>
<td>8.9×10(^{-3})</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) Measured at an initial concentration ([C\(_A\)\(_0\)]) of 0.21 mol/L
\(^b\) Second-order rate constant of reaction
\(^c\) Calculated from Arrhenius plot
illustrated in Scheme 1-2. [22-24] The ionic liquids which have the higher value of dielectric constant react efficiently with AlCl₃ to form chloroaluminate anion. Further, as mentioned above, the polymerization did not proceed in presence of AlCl₃ less than twice equimolar to ionic liquids. The polymerization did not proceed at lower molar ratio of AlCl₃ to ionic liquids because chloroaluminate anion was not formed efficiently. Concerning to the anion, the Lewis basicity and nucleophilicity of anion increase in the following order: OTf⁻ < I⁻ < Cl⁻. [29] The anions of the low Lewis basicity such as OTf⁻ and I⁻ are hard to form chloroaluminate anion as mentioned above. Hence, it is concluded that the ionic liquids having high dielectric constant and an anion of the high Lewis basicity to form the activated species effectively are necessary for preparing high molecular weight F-PEKs. Moreover, since the Lewis acidity of ZnCl₂ and SnCl₄ was lower than that of AlCl₃, [18] these catalysts are hard to form chloroaluminate anion. Immiscibility of ZnCl₂ and SnCl₄ to [C₄mim]Cl is consistent with the formation mechanism of chloroaluminate anion.

Scheme 1-2. Formation of 1-butyl-3-methylimidazolum chloroaluminate anion from [C₄mim]Cl and AlCl₃
Properties of F-PEKs

F-PEK(DPE) and F-PEK(DPB) were characterized as summarized in Table 1-4 with the results of T-PEK(DPE) and I-PEK(DPE) as comparison. The temperatures of 10% weight loss ($T_{d10}$) in nitrogen atmosphere of F-PEK(DPE) and F-PEK(DPB) were over 450°C and they showed excellent thermal stability comparable to T- and I-PEK(DPE). It is noteworthy that F-PEKs possessed high $T_g$ comparable to T- and I-PEK(DPE), whereas much lower $T_m$ than T- and I-PEK(DPE). The $T_g$ and $T_m$ were 161 and 236°C for F-PEK(DPE), 154 and 216°C for F-PEK(DPB), respectively. These values of F-PEKs increase with keto-linkage in main chain and these values are tunable with the ratio of ketone and ether linkage. Although the ratio of $T_m$ to $T_g$ of common polymers is 1.5 to 2.0, [30] that of F-PEK(DPE) and F-PEK(DPB) are 1.17 and 1.14, respectively. Similar phenomenon, which is high $T_g$ and low $T_m$, has been reported for polyesters such as poly(ethylene 2,5-furandicarboxylate). [31] The high $T_g$ of furan-containing polymers are derived from the strong hindrance of furan ring-flipping. [31] It is likely that the ring-flipping of F-PEKs are more highly suppressed than that of T-PEK(DPE). F-PEK(DPE) and F-PEK(DPB) were crystalline polymers as measured by WAXS in Figure 1-14. Solubility of F-PEKs was determined in organic solvents and protic acid at 25°C as shown in Table 1-5. F-PEKs dissolved only in strong acids such as concentrated $\text{H}_2\text{SO}_4$ and TFA, and fluorine-based solvents such as HFIP and 5FPhOH, showing the excellent chemical resistance.
<table>
<thead>
<tr>
<th>Polymer code</th>
<th>K/E&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Solvent</th>
<th>(\eta_{sp}/c)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>(M_n)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>(T_d)&lt;sup&gt;d&lt;/sup&gt;</th>
<th>(T_m)&lt;sup&gt;d&lt;/sup&gt;</th>
<th>(T_m/T_d)&lt;sup&gt;d&lt;/sup&gt;</th>
<th>(T_{10})&lt;sup&gt;e&lt;/sup&gt;</th>
</tr>
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<tbody>
<tr>
<td>F-PEK(DPE)</td>
<td>67/33</td>
<td>[C&lt;sub&gt;4&lt;/sub&gt;mim]Cl</td>
<td>0.31</td>
<td>7.2×10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>161</td>
<td>236</td>
<td>1.17</td>
<td>470</td>
</tr>
<tr>
<td>F-PEK(DPB)</td>
<td>50/50</td>
<td>[C&lt;sub&gt;4&lt;/sub&gt;mim]Cl</td>
<td>0.59</td>
<td>1.3×10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>154</td>
<td>216</td>
<td>1.14</td>
<td>458</td>
</tr>
<tr>
<td>T-PEK(DPE)</td>
<td>67/33</td>
<td>DCE</td>
<td>0.91</td>
<td>1.7×10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>155</td>
<td>384</td>
<td>1.53</td>
<td>527</td>
</tr>
<tr>
<td>I-PEK(DPE)</td>
<td>67/33</td>
<td>DCE</td>
<td>0.98</td>
<td>2.0×10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>153</td>
<td>271</td>
<td>1.28</td>
<td>522</td>
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</tbody>
</table>

<sup>a</sup>Ratio of keto and ether linkage  
<sup>b</sup>Reduced viscosities were measured in 97% H<sub>2</sub>SO<sub>4</sub> at a concentration of 0.1 g/dL and 25°C.  
<sup>c</sup>Number average molecular weight calculated based on end-group analysis.  
<sup>d</sup>\(T_d\) and \(T_m\) recorded on a DSC in nitrogen at a heating rate of 10°C/min in nitrogen.  
<sup>e</sup>Temperature at which 10 % weight loss recorded on a TGA at a heating rate of 10°C/min in nitrogen.
Table 1-5. Solubility of F-PEKs at 25°C

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>DMF</th>
<th>DMAc</th>
<th>NMP</th>
<th>DMSO</th>
<th>H₂SO₄</th>
<th>TFA</th>
<th>TFA/CHCl₃ (9/1)</th>
<th>HFIP</th>
<th>5FPhOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-PEK(DPE)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>F-PEK(DPB)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

*a Insoluble  b Soluble  c Partially soluble*
1-1-4 Conclusions

The Friedel-Crafts polymerizations of FDCC and the aromatic ethers such as DPE and DPB with AlCl₃, ZnCl₂ and SnCl₄ in molecular solvents such as DCE and NB which were a common solvent for the polymerizations did not yield the high molecular weight F-PEKs because of the low affinity of precipitated physical gels among solvent, catalyst and the oligomers. The polymerizations were carried out in various ionic liquids to improve the affinity. The polymerizations proceeded well in [C₄mim]Cl-AlCl₃ mixture, although the obtained F-PEKs contained para-isomer to ether-linkage with the
small amount of ortho-isomer. The gels formed in [C₄mim]Cl was more highly swollen than in DCE and other ionic liquids. In addition, the rate constant estimated by the model reaction of FDCC and anisole was higher in [C₄mim]Cl than that in DCE and NB. The obtained F-PEKs exhibited good thermal stability and chemical resistance comparable to common PEKs and they were crystalline thermoplastic polymers, possessing high glass transition temperature and low melting temperature.

1-1-5 References


1-2 Preparation of Poly(ether ketone) Containing Thiophene-Ring

1-2-1 Introduction

Aromatic PEK containing thiophene-ring (Th-PEK(DPE)) have been synthesized by the Friedel–Crafts polymerization of 2,5-thiophenedicarbonyl dichloride (TDCC) and DPE. [1] However, the molecular weight was not enough high: i.e. the inherent viscosity of Th-PEK(DPE) was 0.11 dL/g. [1]

In previous section, aromatic F-PEKs were synthesized by the Friedel–Crafts polymerization of FDCC and aromatic ethers such as DPE and DPB with AlCl₃. The polymerizations in common molecular solvents such as 1,2-dichloroethane and nitrobenzene did not afford polymers. In contrast, the polymerizations proceeded in specific ionic liquid such as [C₄mim]Cl, and high molecular weight polymers were obtained with good yield due to the enhancement of the reactivity and the degree of swelling of precipitated gels. TDCC was synthesized from 2,5-thiophenedicarboxylic acid (TDCA) which was not bio-based monomer. According to the results of previous section, it was conceivable that the high molecular weight Th-PEK(DPE) could be prepared by TDCC and DPE in [C₄mim]Cl from the viewpoint of polymer chemistry of heterocyclic ring containing PEKs.

This article in this section aims to examine the possibility of preparation of Th-PEK(DPE) by the Friedel-Crafts polymerization of TDCC and DPE in [C₄mim]Cl as depicted in Scheme 1-3.
Scheme 1-3. Synthesis of Th-PEK(DPE) by the Friedel-Crafts polymerization

1-2-2 Experimental

1-2-2-1 Materials

TDCA (TCI Co. Ltd.) was purified by recrystallization from water/methanol (90/10). DPE (Nacalai Tesque Co. Ltd.) was purified by vacuum distillation. DCE (TCI Co. Ltd.) was distilled over calcium hydrate. [C₄mim]Cl (TCI Co. Ltd.) was dehydrated at 100°C for 12 h under 0.3 mmHg prior to use. AlCl₃ (TCI Co. Ltd.), N,N-dimethylformamide (DMF; Sigma Aldrich Co. Ltd.), N,N-dimethylacetamide (DMAc; Sigma Aldrich Co. Ltd.), N-methylpyrrolidone (NMP; Sigma Aldrich Co. Ltd.), dimethyl sulfoxide (DMSO; Sigma Aldrich Co. Ltd.), 97% sulfuric acid (Nacalai Tesque Co. Ltd.), trifluoroacetic acid (TFA; TCI Co. Ltd.), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP; TCI Co. Ltd.) and 2,3,4,5,6-pentafluorophenol (5FPhOH; TCI Co. Ltd.) were used as received.
1-2-2-2 Synthesis of TDCC

TDCC was synthesized from TDCA and thionyl chloride by the previously reported procedure. [2]

1-2-2-3 Polymerization

1-2-2-3-1 Polymerization in DCE

In a 25 mL of three-necked flask equipped with a nitrogen inlet and a stirrer, DPE (0.39 g, 2.3 mmol) and TDCC (0.48 g, 2.3 mmol) were dissolved in DCE (10 mL). The reaction mixture was allowed to cool at -10°C, and AlCl₃ (1.28 g, 9.6 mmol) was added to the mixture under stirring. In this case, the molar ratio of AlCl₃ to FDCC in feed (fᵣ) was 4.2. Then the mixture was stirred at -10°C for 1 h and heated up to 20°C for 0.5 h under dry nitrogen. The polymerization was continued at 20°C for 20-120 h. The mixture was poured into methanol. The precipitates were isolated by filtration and washed with methanol using a Soxhlet extractor for 24 h.

1-2-2-3-2 Polymerization in [C₄mim]Cl

Dehydrated [C₄mim]Cl (10.0g, 57.2 mmol) and AlCl₃ (19.7 g, 148 mmol) were mixed at 20°C for 12 h. DPE (0.39 g, 2.3 mmol), FDCC (0.48 g, 2.3 mmol) and [C₄mim]Cl-AlCl₃ mixture (10 mL, 13.1 g) were placed into a 25 mL three-necked flask
equipped with a nitrogen inlet and a stirrer, and then the mixture was stirred for 10 min at 25°C under dry nitrogen. The polymerization was performed at a given temperature for 24 h. Polymers were collected by the same manner as mentioned above.

1-2-2-4 Measurements and Characterization

Fourier transform infrared (FT-IR) spectra were measured on a FT/IR-410 spectrometer (JASCO Co. Ltd.). Wide angle X-ray scattering (WAXS) patterns were measured on a Gaiger Flex (Rigaku Co. Ltd.) with nickel-filtered Cu-Kα radiation (35 kV, 15 mA). Thermal properties were measured on a Perkin–Elmer TGA-7 (Perkin Elmer Cetus Instruments) at a heating rate of 10°C/min under a nitrogen flow of 20 mL/min. Glass-transition temperature ($T_g$) and melting temperature ($T_m$) were measured on a DSC-8000 (Perkin Elmer Cetus Instruments) at a scanning rate of 10°C/min in nitrogen atmosphere. Reduced viscosities ($\eta_{sp}/c$) were measured with an Ostwald type viscometer at a concentration of 0.1 g/dL in 97% sulfuric acid at 25°C. A solubility test was carried out at 0.05 g/dL in several solvents at 25°C.
1-2-3 Results and Discussion

1-2-3-1 Influence of Solvent on Polymerization

According to the polymerization results of FDCC and DPE in previous section, the polymerizations of TDCC and DPE were carried out in DCE and [C₄mim]Cl at a concentration of 7%. The polymerization concentration was the ratio of the theoretical polymer weight and the solvent. The polymerization temperature was 20°C in DCE and 60°C in [C₄mim]Cl, respectively. Table 1-6 summarized the results of polymerization. The yields and the reduced viscosities of the Th-PEK(DPE) prepared in [C₄mim]Cl were higher than that of Th-PEK(DPE) prepared in DCE. FT-IR spectra are illustrated in Figure 1-15. Although the C=O stretching peak of ketone group was clearly detected at 1633 cm⁻¹, the C=O stretching peak of ester was strongly observed at 1718 cm⁻¹ in the spectrum of Th-PEK(DPE) prepared in DCE. As for Th-PEK(DPE) prepared in

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Time (h)</th>
<th>Temp. (°C)</th>
<th>(f_c)</th>
<th>(\text{[AlCl}_3]/[\text{[C}_4\text{mim}]\text{Cl}]) (mol/mol)</th>
<th>Yield (%)</th>
<th>(\eta_p/c) (dL/g)</th>
</tr>
</thead>
<tbody>
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<td>DCE</td>
<td>20</td>
<td>20</td>
<td>2.8</td>
<td>-</td>
<td>75</td>
<td>0.05</td>
</tr>
<tr>
<td>[C₄mim]Cl</td>
<td>24</td>
<td>60</td>
<td>22</td>
<td>2.6</td>
<td>24</td>
<td>0.25</td>
</tr>
</tbody>
</table>

| \(a\)Polymerizations were carried out at a conc. of 7%. \(b\)Molar ratio of AlCl₃ to TDCC in feed. \(c\)Reduced viscosities were measured in 97% H₂SO₄ at a concentration of 0.1 g/dL and 25°C. \(d\)Impossible to measure due to the low yield.
Figure 1-15. FT-IR spectra of Th-PEK(DPE) prepared in (a) DCE and (b) [C₄mim]Cl

[C₄mim]Cl, although C=O stretching peak of ester was observed at 1711 cm⁻¹, C=O stretching peak of ketone group was clearly detected at 1638 cm⁻¹ in the spectrum of F-PEK(DPE). These results indicated that the polymerization in [C₄mim]Cl-AlCl₃ mixture afforded the high molecular weight PEK as well as the polymerization of FDCC and aromatic ethers. Hence, the Friedel-Crafts polymerizations in ionic liquids are a new approach to expand possibility of polymer synthesis such as preparation of PEKs containing heterocyclic rings.
1-2-3-2 Properties of Th-PEK(DPE)

Figure 1-16 showed the WAXS profile of Th-PEK(DPE). Unlike F-PEK(DPE), Th-PEK(DPE) was amorphous. Thermal properties of Th-PEK(DPE) were measured by a DSC and TGA as summarized in Table 1-7. Th-PEK(DPE) possessed 154°C of \( T_g \) and it did not exhibit melting temperature. Although the molecular weight of Th-PEK(DPE) was enough high, it possessed high glass transition temperature. The temperatures of 10% weight loss (\( T_{d10} \)) in nitrogen atmosphere of Th-PEK(DPE) was over 420°C and they showed excellent thermal stability comparable to aromatic PEKs. F-PEK(DPE) and F-PEK(DPB) were crystalline polymers as measured by WAXS in Figure 1-14.
Solubility of Th-PEK (DPE) was determined in organic solvents and protic acid at 25°C as shown in Table 1-8. It dissolved only in strong acids such as concentrated H$_2$SO$_4$ and TFA, and fluorine-based solvents such as HFIP and 5FPhOH, showing the excellent chemical resistance.

<table>
<thead>
<tr>
<th>DMF</th>
<th>DMAc</th>
<th>NMP</th>
<th>DMSO</th>
<th>H$_2$SO$_4$</th>
<th>TFA</th>
<th>TFA/CHCl$_3$ (9/1)</th>
<th>HFIP</th>
<th>5FPhOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

*a Insoluble  
*b Soluble  
*c Partially soluble

Table 1-7. Thermal Properties of Th-PEK

<table>
<thead>
<tr>
<th>$\eta_{sp}/c$</th>
<th>$T_g$</th>
<th>$T_m$</th>
<th>$T_{d10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(dL/g)</td>
<td>(°C)</td>
<td>(°C)</td>
<td>(°C)</td>
</tr>
<tr>
<td>0.25</td>
<td>154</td>
<td>Not detected</td>
<td>428</td>
</tr>
</tbody>
</table>

*a Reduced viscosities were measured in 97% H$_2$SO$_4$ at a concentration of 0.1 g/dL and 25°C.  
*b $T_g$ and $T_m$ recorded on a DSC in nitrogen at a heating rate of 10°C/min in nitrogen.  
*c Temperature at which 10 % weight loss recorded on a TGA at a heating rate of 10°C/min in nitrogen.

Table 1-8. Solubility of Th-PEK(DPE) at 25°C
1-2-4 Conclusions

The Friedel-Crafts polymerizations of TDCC, which was not bio-based monomer, and DPE were carried out in DCE and [C$_4$ mim]Cl- AlCl$_3$ mixture from the viewpoint of polymer chemistry of heterocyclic ring containing PEKs. Although the polymerizations in DCE yielded low molecular weight PEK, that in [C$_4$ mim]Cl-AlCl$_3$ mixture afforded the high molecular weight Th-PEK(DPE) as well as the polymerization of FDCC and aromatic ethers. This fact indicated that the[C$_4$ mim]Cl-AlCl$_3$ mixture possess a potential to prepare PEKs containing heterocyclic rings and to expand possibility of polymer synthesis. The obtained Th-PEK(DPE) exhibited good thermal stability and chemical resistance comparable to common PEKs like F-PEKs.

1-2-5 References


CHAPTER 2

PREPARATION OF AROMATIC POLY(ETHER KETONE)S BY
NUCLEOPHILIC AROMATIC SUBSTITUTION POLYCONDENSATION

2-1 Introduction

In previous Chapter, it was found that the electrophilic aromatic substitution polymerization of FDCC and aromatic ethers did not yield furan ring containing PEKs (F-PEKs) in molecular solvents like 1,2-dichloroethane, but the polymerization in ionic liquid gave high molecular F-PEKs. However, the mechanical properties of these F-PEKs had not been measured because the molecular weight was not enough high to prepare tough films. It is necessary to synthesize high molecular weight F-PEKs for characterization to estimate the potential for high-performance polymers with the comparison of common PEKs. As aforesaid, preparations of PEKs are classified into two reactions. One is the Friedel-Crafts polymerization which was discussed in Chapter 1 to form the ketone linkages. Another is the nucleophilic aromatic substitution polymerization between activated aromatic dihalides and alkali metal phenoxides to form the ether linkage. [1-3] Therefore, it is conceivable that F-PEKs can be prepared
by the nucleophilic aromatic substitution polymerization of aromatic dihalides and aromatic bisphenols. Moreover, this polymerization can provide the wide variety of the PEKs because of the structural diversity of aromatic bisphenols.

This work aims to synthesize bio-based high molecular weight F-PEKs by the nucleophilic aromatic substitution polymerization of 2,5-bis(4-fluorobenzoyl)furan (BFBF) derived from FDCA and potassium salts of aromatic bisphenols as shown in Scheme 2-1, and to characterize them.

2-2 Experimental

2-2-1 Materials

FDCA (TCI Co. Ltd.) was recrystallized from water. Fluorobenzene (TCI Co. Ltd.) was distilled over calcium hydrate. 4,4’-Dihydroxydiphenylether (H-DPE; TCI Co. Ltd.) and 4,4’-dihydroxybenzophenone (H-BP; TCI Co. Ltd.) were recrystallized from methanol/water (50/50). Hydroquinone (HQ; TCI Co. Ltd.), resorcinol (RC; TCI Co. Ltd.), 4,4’-thiobisbenzenethiol (TBT; TCI Co. Ltd.) and terephthaloyl chloride (TCI Co. Ltd) were purified by the sublimation. p-Methoxyphenol (PMP; TCI Co. Ltd.), 2,2’-bis(4-hydroxyphenyl)propane (BA; TCI Co. Ltd.) and 2,2-bis(4-hydroxyphenyl)hexafluoropropane (6FBA; TCI Co. Ltd.) were recrystallized from toluene. Diphenyl sulfone (DPS; TCI Co. Ltd.) was recrystallized
Scheme 2-1. Preparation of F-PEKs from BFBF and aromatic bisphenols
from methanol/water (95/5). AlCl$_3$ (TCI Co. Ltd.), N-methylpyrrolidone (NMP; Sigma Aldrich Co. Ltd.), 97% sulfuric acid (Nacalai Tesque Co. Ltd.), potassium carbonate ($\text{K}_2\text{CO}_3$; Wako Co. Ltd.), $N,N$-dimethylformamide (DMF; Sigma Aldrich Co. Ltd.), $N,N$-dimethylacetamide (DMAc; Sigma Aldrich Co. Ltd.), 1,3-dimethyl-2-imidazolidinone (DMI; Sigma Aldrich Co. Ltd.), methyl ethyl ketone (MEK; Nacalai Tesque Co. Ltd.), trifluoroacetic acid (TFA; TCI Co. Ltd.) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP; TCI Co. Ltd.) were used as received.

2-2-2 Synthesis of Aromatic Bisfluorides

BFBF was synthesized by the Friedel-Crafts reaction of FDCC and fluorobenzene with aluminum chloride. FDCC was synthesized from FDCA and thionyl chloride by the previously reported procedure. [4] FDCC were purified by recrystallization from $n$-hexane, and following sublimation at 0.2 mmHg. FDCC (5.00 g, 25.9 mmol) and fluorobenzene (7.47 g, 77.7 mmol) were placed into a 50 mL three-necked flask equipped with a condenser and gas inlet and outlet tubes. The mixture was allowed to cool at 0°C, and AlCl$_3$ (9.67 g, 72.5 mmol) was added to the mixture. The reaction mixture was stirred at 0°C for 1 h and heated up to 70°C over 1 h. Then, the reaction was carried out at 70°C for 12 h. After the reaction, the mixture was allowed to cool and poured into methanol. Precipitates were filtrated, and washed by 1N hydrochloric acid and water several times. Solids obtained were subsequently recrystallized from
toluene/n-hexane (1/1) and dried under vacuum at 50°C. BFBF white crystals (7.20 g) were obtained with the yield of 89%. Elemental analysis calculated for C₁₈H₁₀O₃F₂: C 69.23%, H 3.22%; found: C 69.31 %, H 2.94 %. Mp 171°C, FT-IR (KBr): ν = 1646 (vs), 1599 (s), 1556 (m), 1506 (m), 1239 (s), 1H-NMR (300 MHz, DMSO-d₆, δ): 7.48 (t, J = 7 Hz, 4H, Ar H), 7.59 (s, 2H, Ar H), 8.11 (t, J = 7 Hz, 4H, Ar H). 1,4-Bis(4-fluorobenzoyl)benzene (BFBB) was also prepared from terephthaloyl chloride and fluorobenzene by the previously reported procedure. [5]

2-2-3 Model Reaction

PMP (0.95 g, 7.6 mmol), K₂CO₃ (1.06 g, 7.6 mmol), NMP (10.0 g) and dehydrated toluene (10 mL) were added into a 25 mL of three-necked flask equipped with a nitrogen inlet tube and a stirrer. The mixture was refluxed for 1 h to form potassium salt of PMP by azeotropic distillation. BFBF (1.20 g, 3.8 mmol) was added to the mixture and the mixture was stirred at 150°C for 0.5 h. Then, the mixture was allowed to cool at 20°C and poured into water/methanol (95/5). Precipitates were collected by filtration and washed with water/methanol (95/5) several times to remove unreacted PMP and K₂CO₃. The model reactions of BFBB and PMP were also carried out by the same manner.
2-2-4 Polymerization

The polymerization of BFBF and H-DPE was described as a typical procedure. H-DPE (1.07 g, 5.3 mmol), K$_2$CO$_3$ (1.53 g, 11.1 mmol), NMP (10.0 g) and dehydrated toluene (10 mL) were added into a 25 mL of three-necked flask equipped with a nitrogen inlet tube and a stirrer. The mixture was refluxed for 1 h to form potassium salt of H-DPE by azeotropic distillation. The mixture was allowed to cool at 80°C and BFBF (1.65 g, 5.3 mmol) was added to the mixture. Then, the mixture was stirred at 150°C for 0.5 h and heated up to 200°C under dry nitrogen. The polymerization was continued at 200°C for 0.5-11.5 h. After the polymerization, the mixture was allowed to cool at 20°C and poured into methanol. Precipitates were collected by filtration, and washed with 0.5N hydrochloric acid and water several times. Thereafter, the precipitates were washed with methanol/toluene (90/10) using a Soxhlet extractor for 24h.

2-2-5 Measurements and Characterization

Fourier transform infrared (FT-IR) spectra were measured on a FT/IR-410 spectrometer (JASCO Co. Ltd.). 300 MHz $^1$H-NMR spectra were obtained on a Varian Unity-500 spectrometer in CDCl$_3$. Wide angle X-ray scattering (WAXS) patterns were measured on a Gaiger Flex (Rigaku Co. Ltd.) with nickel-filtered Cu-Ka radiation (35 kV, 15 mA). Thermal properties were measured on a Perkin–Elmer TGA-7 (Perkin
Elmer Cetus Instruments) at a heating rate of 20°C/min under a nitrogen flow of 20 mL/min. Glass-transition temperature ($T_g$) and melting temperature ($T_m$) were measured on a DSC-8000 (Perkin Elmer Cetus Instruments) at a scanning rate of 20°C/min in nitrogen atmosphere. Reduced viscosities ($\eta_{sp}/c$) were measured with an Ostwald type viscometer at a concentration of 0.2 g dL$^{-1}$ in 97% sulfuric acid at 25°C. A solubility test was carried out at 0.05 g dL$^{-1}$ in several solvents at 25°C. Tensile tests were performed at 25°C on a STA-1150 (Orientec Co. Ltd.) with a crosshead speed of 1.0 mm min$^{-1}$. The specimens for tensile testing (size 100 × 10 × 0.5-0.6 mm) were cut from the films prepared by melt-press. The tensile strength was obtained from the stress at break, and elongation at break was determined by the initial length of the specimens (30 mm). These tensile properties were average values of three measurements.

2-3 Results and Discussion

2-3-1 Model Reaction and Kinetics

The nucleophilic aromatic substitution reaction proceeded under addition-elimination mechanism with forming a Meisenheimer complex as intermediate. [6-9] The reactivity of halide monomers having electron withdrawing groups at ortho- or para-position to carbons attached halogens is enhanced to the nucleophilic attack by phenoxide. [10] In case of BFBF, it was inferred that the nucleophilic attack of phenoxide to carbon of C-F bond is slightly suppressed due to the $\pi$-electron rich furan-ring. Therefore, the model
reaction of BFBF and potassium salt of PMP was carried out in NMP at 150°C to clarify the reactivity of BFBF for nucleophilic aromatic substitution reactions as shown in Scheme 2-2. BFBB was also used to compare the reactivity. The reactions were kinetically followed by $^1$H-NMR measurements. Figure 2-1 showed the spectral change with reaction time. The spectra show a multiplet at about 7.4 ppm for the furan ring protons. Ortho- and meta-protons to C-F bonds which were unreacted residue were assigned at 7.23 and 8.16 ppm. Ortho- and meta-protons to ether linkages were seen at 6.9 to 7.1 and 8.10 ppm. Signal intensities of ortho- and meta-protons to C-F bond decreased with time. In contrast, signal intensities derived from ortho- and meta-protons to formed ether linkage increased with time. Figure 2-2 showed the plot of the second-order kinetic reaction and the rate constants ($k_2$) were estimated from the slopes. The $k_2$ value of the reaction of BFBF and PMP and that of BFBB and PMP were
6.1×10^{-2} and 1.5×10^{-1} \text{ L mol}^{-1} \text{ min}^{-1}, respectively. The reactivity of BFBF was lower than that of BFBB, but the extent of reaction of BFBF was approximately 85% at 30 min.

**Figure 2-1.** Change in $^1$H-NMR spectra of the model reaction of BFBF and PMP with reaction time
Figure 2-2. Second order kinetic plots of the model reaction of (●) BFBF and (○) BFBB with PMP at 150°C

Figure 2-3. FT-IR spectrum of product prepared from BFBF and PMP for 30 min
Furthermore, C=O stretching peak of ketone and C-O stretching peak of ether were clearly observed at 1644 cm$^{-1}$ and 1260 cm$^{-1}$ in the spectrum of product as shown in Figure 2-3. These results indicated that BFBF possessed enough reactivity for nucleophilic aromatic substitution reactions with the phenoxide.

2-3-2 Polymerizations

The nucleophilic aromatic substitution polymerizations were usually carried out in aprotic polar solvents such as NMP and DPS with slight excess of catalyst such as K$_2$CO$_3$ to bisphenols. [1, 2, 11] In general, the molar ratio of K$_2$CO$_3$ to bisphenol ([K$_2$CO$_3$]/[Bisphenol]) was suitable to be about 2.2, and it was also desirable to carry out the polymerization under higher monomer concentration condition. [1, 2] According to both these previous studies and the results of the model reaction, the polymerizations of BFBF and H-DPE were carried out in NMP and DPS with changing time, concentration and [K$_2$CO$_3$]/[H-DPE]. F-PEKs synthesized in this study were described by using bisphenols; for example, F-PEK synthesized from BFBF and H-DPE was abbreviated as F-PEK(H-DPE). The polymerizations were performed at 150$^\circ$C for 0.5 h and then at 200$^\circ$C for 0.5-11.5 h. Table 2-1 summarized polymerization results. The polymerization proceeded well for several hours with slight excess of K$_2$CO$_3$ to H-DPE in NMP and DPS. The reduced viscosities of F-PEK(H-DPE) gave maximum value at 1 h in NMP and at 3 h in DPS. Although the polymerization at the lower concentration of
10% afforded polymers with good yield, the reduced viscosity was lower than that of polymers prepared at higher concentration. The obtained F-PEK(H-DPE) turned out to be partially insoluble in sulfuric acid with time. The weight percentage of the soluble part in sulfuric acid to as prepared polymer ($W_s$) decreased gradually with time. The reduced viscosities also decreased with time. The FT-TR spectra of F-PEK(H-DPE) prepared in NMP for 3 h were illustrated in Figure 2-4. Although the C=O stretching band of ketone group and the C-O stretching band of ether group were observed at 1642 cm$^{-1}$ and ca. 1260 cm$^{-1}$ in both spectra of soluble and insoluble parts in sulfuric acid, the O-H stretching band of hydroxyl group was clearly observed at ca. 3200 cm$^{-1}$ in the spectrum of insoluble parts. It is known that several side reactions occurred for the nucleophilic aromatic substitution reactions. [1, 2] For instance, the phenoxide abstract a proton from a halide-activated aromatic ring to give a carbanion and a phenol residue, and the carbanion reacts continuously with carbonyl group or aromatic rings. [1] Additionally, depolymerization occurs by the attack of fluoride anion of by-produced potassium fluoride to the ether linkages. [14] These side reactions result in the formation of branching structures and the reduction of molecular weight. In case of the polymerizations of BFBF and H-DPE, these side reactions might occur, bringing about the formation of some defect structure and the reduction of molecular weight during the longer polymerization.

The polymerizations of BFBF and other aromatic bisphenols were also carried out in NMP at a [K$_2$CO$_3$]/[Bisphenol] of 2.1. Table 2-2 summarized polymerization results.
Table 2-1. Syntheses of F-PEK(H-DPE) under various conditions $^a$

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Conc. (%)</th>
<th>Time $^b$ (h)</th>
<th>$[\text{K}_2\text{CO}_3]/[\text{H-DPE}]$ (mol/mol)</th>
<th>Yield $^c$ (%)</th>
<th>$W_s$ $^d$ (wt%)</th>
<th>$\eta_{sp}/c$ $^e$ (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMP</td>
<td>10</td>
<td>0.5</td>
<td>2.2</td>
<td>85</td>
<td>100</td>
<td>0.40</td>
</tr>
<tr>
<td>NMP</td>
<td>25</td>
<td>0.5</td>
<td>2.0</td>
<td>95</td>
<td>100</td>
<td>0.87</td>
</tr>
<tr>
<td>NMP</td>
<td>25</td>
<td>0.5</td>
<td>2.1</td>
<td>97</td>
<td>100</td>
<td>1.27</td>
</tr>
<tr>
<td>NMP</td>
<td>25</td>
<td>2.5</td>
<td>2.2</td>
<td>97</td>
<td>100</td>
<td>1.24</td>
</tr>
<tr>
<td>NMP</td>
<td>25</td>
<td>11.5</td>
<td>2.2</td>
<td>90</td>
<td>87</td>
<td>0.93</td>
</tr>
<tr>
<td>NMP</td>
<td>25</td>
<td>2.5</td>
<td>2.2</td>
<td>88</td>
<td>59</td>
<td>0.80</td>
</tr>
<tr>
<td>DPS</td>
<td>25</td>
<td>0.5</td>
<td>2.2</td>
<td>49</td>
<td>100</td>
<td>0.12</td>
</tr>
<tr>
<td>DPS</td>
<td>25</td>
<td>2.5</td>
<td>2.0</td>
<td>89</td>
<td>100</td>
<td>0.62</td>
</tr>
<tr>
<td>DPS</td>
<td>25</td>
<td>2.5</td>
<td>2.1</td>
<td>95</td>
<td>100</td>
<td>0.81</td>
</tr>
<tr>
<td>DPS</td>
<td>25</td>
<td>2.5</td>
<td>2.2</td>
<td>98</td>
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<td>DPS</td>
<td>25</td>
<td>11.5</td>
<td>2.2</td>
<td>89</td>
<td>97</td>
<td>0.56</td>
</tr>
</tbody>
</table>

$^a$ Polymerizations were carried out at 150°C for 0.5 h and then 200°C.

$^b$ Polymerization time at 200°C.

$^c$ After washing with methanol/toluene (90/10) using a Soxhlet extractor

$^d$ Soluble parts in 97% H$_2$SO$_4$

$^e$ Reduced viscosities of soluble parts were measured in 97% H$_2$SO$_4$ at a concentration of 0.20 g/dL and 25°C.
The nucleophilicity of thiophenoxide was higher than that of other phenoxides, and therefore the polymerization of BFBF and TBT was carried out at 100°C. In all cases, the F-PEKs were obtained with good yields. The C=O stretching band of ketone group and the C-O stretching band of ether group were observed clearly at 1640-1650 cm\(^{-1}\) and 1250-1260 cm\(^{-1}\) by FT-IR measurement as shown in Figure 2-5. Insoluble parts in sulfuric acid were very low. Since it was conceivable that the nucleophilicity of bisphenoxide of H-BP, BA, 6FBA, HQ, RC was lower than H-DPE, the reduced viscosities of them were lower than that of F-PEK(H-DPE). With respect to F-PEK(TBT), the polymerization was carried out at lower temperature, which resulted in the lower reduced viscosity.
**Table 2-2.** Polymerizations of BFBF and various aromatic bisphenols

<table>
<thead>
<tr>
<th>Polymer code</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>$W_s$ (wt%)</th>
<th>$\eta_{sp}$/c (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-PEK(H-BP)</td>
<td>0.5</td>
<td>85</td>
<td>100</td>
<td>0.40</td>
</tr>
<tr>
<td>F-PEK(BA)</td>
<td>0.5</td>
<td>101</td>
<td>100</td>
<td>0.11</td>
</tr>
<tr>
<td>F-PEK(6FBA)</td>
<td>0.5</td>
<td>96</td>
<td>&gt;99</td>
<td>0.54</td>
</tr>
<tr>
<td>F-PEK(HQ)</td>
<td>0.5</td>
<td>93</td>
<td>&gt;99</td>
<td>0.52</td>
</tr>
<tr>
<td>F-PEK(RC)</td>
<td>0.5</td>
<td>97</td>
<td>95</td>
<td>0.21</td>
</tr>
<tr>
<td>F-PEK(TBT)</td>
<td>1.0</td>
<td>92</td>
<td>100</td>
<td>0.11</td>
</tr>
</tbody>
</table>

$^a$ Polymerizations were carried out at 150°C for 0.5 h and then 200°C in NMP.

$^b$ Polymerization time at 200°C.

$^c$ The polymerization was carried out at 100°C for 1 h in NMP.

$^d$ After washing with methanol/toluene (90/10) using a Soxhlet extractor

$^e$ Soluble parts in 97% H$_2$SO$_4$

$^f$ Reduced viscosities of soluble parts were measured in 97% H$_2$SO$_4$ at a concentration of 0.20 g/dL and 25°C.
Figure 2-5 FT-IR spectra of (a) F-PEK(H-BP), (b) F-PEK(BA), (c) F-PEK(6FBA), (d) F-PEK(HQ), (e) F-PEK(RC), and (f) F-PEK(TBT)
2-3-3 Characterization of F-PEKs

Figure 2-6 showed the WAXS intensity profiles of F-PEKs. Except for F-PEK(BA) and F-PEK(RC), F-PEKs were semicrystalline polymers. F-PEK(H-DPE), F-PEK(H-BP) and F-PEK(HQ) showed similar diffraction patterns. As for F-PEK(H-DPE), it shew five diffraction peaks as followed; \( \theta = 19.1^\circ, 20.3^\circ, 21.9^\circ, 23.7^\circ \) and \( 29.5^\circ \). The diffraction patterns F-PEK(TBT) and F-PEK(6FBA) were different from those of F-PEK(H-DPE). The peaks appeared at lower angle such as \( \theta = 16.5^\circ \) for F-PEK(TBT) and \( 20 = 14.3^\circ \) and \( 17.2^\circ \) for F-PEK(6FBA). It is conceivable that the packing of these F-PEKs is loosened due to the bulkiness of the \( 1,1,1,3,3,3 \)-hexafluoroisopropylidene group and the thioether group. Thermal properties of F-PEKs were characterized as summarized in Table 2-3. The temperatures of 10% weight loss \( (T_{d10}) \) in nitrogen atmosphere of F-PEK(DPE) and F-PEK(DPB) were over 440ºC and they showed excellent thermal stability. \( T_g \) and \( T_m \) of F-PEKs were tunable with the structure of bisphenoxide. \( T_g \) of F-PEK(HQ) and F-PEK(TBT) could not be detected with changing scanning rate of DSC measurements. F-PEK (F-PEK(HQ')) had been prepared by the electrophilic aromatic substitution polymerization of FDCC and DPB in Chapter 1. It was the same polymer structure as F-PEK(HQ) prepared in this study. \( T_m \) of F-PEK(HQ') was 216ºC, which was much lower than that of F-PEK(HQ). In case of the electrophilic aromatic substitution reaction, FDCC reacted with \( p \)-position carbons to the ether linkage DPB mainly, but it did often with \( o- \).
Figure 2-6. WAXS intensity profiles of (a) F-PEK(H-DPE), (b) F-PEK(H-BP), (c) F-PEK(TBT), (d) F-PEK(BA), (e) F-PEK(6FBA), (f) F-PEK(HQ) and (g) F-PEK(RC)
position carbons to ether linkage. The non-linear defect structure brought about reduction of $T_m$. Tensile properties of undrawn film of F-PEK(H-DPE) prepared by melt-press were measured. The stress-strain curve of undrawn F-PEK(H-DPE) film which was 550 μm in thickness was illustrated in Figure 2-7. The tensile strength ($\sigma$) and elongation ($\varepsilon$) at break of the film were 78.0 MPa and 6.2%. The tensile modulus ($E$) was 1.2 GPa. It was reported that commercial available poly(ether ether ketone) possessed 97 MPa of $\sigma$, 60 % of $\varepsilon$ and 3.5 GPa of $E$. [15] Although F-PEK(H-DPE) film was more brittle than the commercially available poly(ether ether ketone), it possessed

<table>
<thead>
<tr>
<th>Polymer code</th>
<th>$T_g , ^{a}$ (°C)</th>
<th>$T_m , ^{a}$ (°C)</th>
<th>$T_{d10} , ^{b}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-PEK(H-DPE)</td>
<td>135</td>
<td>280</td>
<td>477</td>
</tr>
<tr>
<td>F-PEK(H-BP)</td>
<td>143</td>
<td>337</td>
<td>450</td>
</tr>
<tr>
<td>F-PEK(BA)</td>
<td>111</td>
<td>ND</td>
<td>449</td>
</tr>
<tr>
<td>F-PEK(6FBA)</td>
<td>109</td>
<td>199</td>
<td>470</td>
</tr>
<tr>
<td>F-PEK(HQ)</td>
<td>ND</td>
<td>293</td>
<td>494</td>
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<tr>
<td>F-PEK(RC)</td>
<td>159</td>
<td>ND</td>
<td>448</td>
</tr>
<tr>
<td>F-PEK(TBT)</td>
<td>ND</td>
<td>263</td>
<td>467</td>
</tr>
</tbody>
</table>

$^{a}$ Glass transition and melting temperature were recorded on a DSC with a scanning rate of 20°C/min.
$^{b}$ Temperature at which 10 % weight loss recorded on a TGA at a heating rate of 20°C/min in nitrogen.
$^{c}$ Not detected
good mechanical properties comparable to common high performance polymers. Table 2-4 presented solubility of F-PEKs in organic solvents and protic acid at 25°C. F-PEK(H-DPE), F-PEK(H-BP), F-PEK(HQ) and F-PEK(TBT) were dissolved in concentrated H₂SO₄ easily, but they were inert against organic solvents. They possessed the excellent chemical resistance. In contrast, F-PEK(BA), F-PEK(6FBA) and F-PEK(RC) dissolved not only concentrated H₂SO₄ but also some organic solvents. The solubility of F-PEKs was tunable with the structure of bisphenols.

**Figure 2-7.** Stress-strain curve of undrawn F-PEK(H-DPE) film (thickness: 550 μm)


2-4 Conclusions

Although the reactivity for the nucleophilic aromatic substitution reaction of BFBF was lower than that of the homologue BFBB, the model reaction of BFBF and PMP in presence of $K_2CO_3$ as a catalyst formed the ether linkage with good conversion. Taking the results of reactivity into account, the polymerizations of BFBF and aromatic bisphenols in presence of $K_2CO_3$ were carried out in aprotic polar solvents. The polymerizations afforded F-PEKs with good yields. The longer polymerization time brought about the formation of insoluble parts in sulfuric acid and the reduction of

<table>
<thead>
<tr>
<th>Polymer code</th>
<th>DMF</th>
<th>DMAC</th>
<th>$H_2SO_4$</th>
<th>TFA</th>
<th>HFIP</th>
<th>DME</th>
<th>MEK</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-PEK(H-DPE)</td>
<td>$^+$</td>
<td>$^- b$</td>
<td>$^+ c$</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>F-PEK(H-BP)</td>
<td>$-$</td>
<td>$-$</td>
<td>$+$</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>F-PEK(BA)</td>
<td>$^+$</td>
<td>$^+$</td>
<td>$+$</td>
<td>$^+$</td>
<td>$^+$</td>
<td>$^+$</td>
<td>$^+$</td>
</tr>
<tr>
<td>F-PEK(6FBA)</td>
<td>$-$</td>
<td>$^+$</td>
<td>$+$</td>
<td>$^+$</td>
<td>$^+$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>F-PEK(HQ)</td>
<td>$-$</td>
<td>$-$</td>
<td>$+$</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>F-PEK(RC)</td>
<td>$^+$</td>
<td>$^+$</td>
<td>$+$</td>
<td>$^+$</td>
<td>$^+$</td>
<td>$^+$</td>
<td>$^+$</td>
</tr>
<tr>
<td>F-PEK(TBT)</td>
<td>$-$</td>
<td>$-$</td>
<td>$+$</td>
<td>$^+$</td>
<td>$^+$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
</tbody>
</table>

$^a$ Partially soluble $^b$ Insoluble $^c$ Soluble

Table 2-4. Solubility of F-PEKs at 25°C
molecular weights. F-PEKs were semicrystalline polymers with the exception of F-PEK(BA) and F-PEK(RC). The obtained F-PEKs exhibited good thermal stability, mechanical properties and chemical resistance comparable to common high performance polymers. The thermal properties such as melting and glass transition temperature were tunable with the structures of bisphenols.

2-5 References


CHAPTER 3

PREPARATION OF WHOLLY AROMATIC POLYESTERS FROM
2,5-FURANDICARBOXYLIC ACID AND AROMATIC DIACETATES

3-1 Introduction

Wholly aromatic polyesters (PEss) are industrially used as high performance engineering materials. [1, 2] In particular, thermotropic liquid-crystalline PEss possess excellent thermal stability, mechanical properties and processability. [2, 3] However, they have been prepared from petroleum-based aromatic monomers such as terephthalic acid (TPA), \( p \)-hydroxybenzoic acid, hydroquinone, 6-hydroxy-2-naphtoic acid and so on. [1, 2] From the viewpoint of the suppression of the petroleum consumption to develop the sustainable development society, it is of great importance to replace the monomers from the petroleum-based materials to the biomass-based materials which are renewable, resulting in the reduction of the ratio of petroleum-based moiety in the polymers. FDCA prepared from cellulose and glucose has been attracted attention as a bio-based monomer comparable or substitutable to aromatic dicarboxylic acids like TPA, isophthalic acid (IPA) and 2,6-naphthalenedicarboxylic acid. Recently, it has been reported that poly(ethylene 2,5-furandicarboxylate) synthesized from FDCA exhibited
good thermal properties comparable to the poly(ethylene terephthalate). [4,5] It is conceivable that FDCA possesses enough potential for monomers of high performance polymers. Many studies have focused on syntheses of polyesters from FDCA [4-16]. Although wholly aromatic PEs has been synthesized by the interfacial polymerization of 2,5-furandicarbonyl dichloride and hydroquinone [5], few investigations has been reported on the detailed properties such as mechanical properties of furan-based polyesters [14,17].

In this Chapter, this work aims to synthesize PEss (F-PEss) from FDCA and petroleum-based aromatic diacetates such as 1,3-/1,4-diacetoxybenzene (DAB) as illustrated in Scheme 3-1 and to characterize them with the comparison of PEss prepared from TPA, IPA and 2,5-thiophendicarboxylic acid (TDCA).

![Scheme 3-1. Preparation of PEss from dicarboxylic acids and aromatic diacetates](image)

91
3-2 Experimental

3-2-1 Materials

FDCA (TCI Co. Ltd.) was purified by recrystallization from water. TPA and IPA (Sigma Aldrich Co. Ltd.) were purified by the sublimation. TDCA (TCI Co. Ltd.) was purified by recrystallization from water/methanol (80/20). 1,3-DAB (TCI Co. Ltd.) and diphenyl ether (DPE, Nacalai Tesque Co. Ltd.) were purified by vacuum distillation. 1,4-DAB (TCI Co. Ltd.) was purified by recrystallization from ethyl acetate/n-hexane (20/80).

3-2-2 Polymerizations

All polyesters were prepared by the transesterification of the dicarboxylic acids and the diacetates without a catalyst.

3-2-2-1 Solution Polymerization

FDCA (1.00 g; 6.4 mmol), DAB (1.25 g; 6.4 mmol) and DPE (30.4 mL) were placed into a three necked flask equipped with a Liebig condenser and gas inlet and outlet tubes. The molar ratio of 1,4-DAB in feed (χ) described as follows: χ (mol%) = [1,4-DAB]/([1,3+DAB]+ [1,4-DAB])×100. The reaction mixture was heated up to
240°C and refluxed at 240°C for 6 h with stirring under nitrogen. DPE was distillated at 10 mmHg. The reaction temperature was raised to 270°C and kept at 270°C for 3 h under vacuum (0.1-0.3 mmHg). The obtained polymers were washed with acetone and methanol.

3-2-2-2 Kinetics of Solution Polymerization

FDCA (0.50 g; 3.2 mmol) and DPE (15.2 mL) were placed into a 25mL three necked flask equipped with gas inlet and outlet tubes, and a stirrer. The mixture was heated up to a predefined temperature with under nitrogen flow. DAB (0.62 g; 3.2 mmol) was added to the mixture and the mixture was kept at the temperature. Eliminated acetic acid which was a by-product was trapped in the water and titrated with 0.05 mol L⁻¹ sodium hydroxide solution.

3-2-2-3 Bulk and Solid State Polymerization

FDCA (2.00 g; 12.8 mmol) and DAB (2.49 g; 12.8 mmol) were placed into a three necked flask equipped with a Liebig condenser and gas inlet and outlet tubes. The reaction mixture was heated up to 230°C with stirring under nitrogen. It was heated to 250°C at a heating rate of 10°C/h and subsequently kept at 250°C for 4 h under nitrogen. The mixture was pulverized, and subsequently heated up to 270°C and kept at 270°C for
6 h under vacuum (0.1-0.3 mmHg). The obtained polymers were washed with acetone and methanol. In case of TPA, IPA and TDCA as dicarboxylic acid, the polymerizations were carried out in the similar manner.

3-2-3 Measurements and Characterization

Fourier transform infrared (FT-IR) spectra were measured on a FT/IR-410 spectrometer (JASCO Co. Ltd.). 300 MHz \(^1\)H-NMR was measured on a Varian Unity-500 spectrometer in DMSO-\(d_6\). Wide angle X-ray scattering (WAXS) patterns were measured on a Gaiger Flex (Rigaku Co. Ltd.) with nickel-filtered Cu-K\(\alpha\) radiation (35 kV, 15 mA). Tensile tests were performed at 25°C on a STA-1150 (Orientec Co.) with a crosshead speed of 1.0 mm/min. The specimens (size 50 \(\times\) 10 \(\times\) 0.3–0.4 mm) for tensile testing were cut from the films. The tensile strength was obtained from the stress at break, and elongation at break was determined by the initial length of the specimens (20 mm). These tensile properties were the average of three specimens. The viscoelastic properties were measured on a Rheovibron DDV-01FP (Orientec Co. Ltd.) at a frequency of 10 Hz in the temperature range of -150 to 250°C at a heating rate of 3°C/min. Thermal properties were measured on a Perkin–Elmer TGA-7 (Perkin Elmer Cetus Instruments) at a heating rate of 10°C/min under a nitrogen flow of 20 mL/min. Glass transition temperature and melting temperature were measured on a DSC-8000 (Perkin Elmer Cetus Instruments) at a scanning rate of 10°C/min in nitrogen atmosphere.
The softening temperature from solid phase \( (T_{k\rightarrow s}) \) was measured on a micro melting point apparatus MP-500D (Yanako Co.) at a heating rate of 5°C/min. Polarizing microscopy (POM) was performed with a heating rate of 5°C/min to determine the transition temperature from nematic to isotropic phase \( (T_{N\rightarrow I}) \) with an Olympus microscope (BX-50) equipped with a Linkam hot stage. Matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a Bruker Daltonics AutoFLEX MALDI-TOF MS system operating with a 337 nm N\(_2\) laser. Spectra were obtained in the linear positive mode with an accelerating potential of 20 kV. Mass calibration was performed with angiotensin I (M.W. 1296.69) and insulin B (M.W. 3496.96) from a Sequzyme peptide mass standard kit. Samples were then prepared by the evaporation-grinding method and ran in 1,8-dihydroxy-9(10H)-anthracenone as a matrix doped with potassium trifluoroacetate. Reduced viscosity was measured with an Ostwald type viscometer at a concentration of 0.1 g dL\(^{-1}\) in acetone at 25°C.

3-3 Results and Discussion

3-3-1 Solution Polymerizations in DPE

It has been hardly reported that the polymerization of FDCA and acetate compounds by the transesterification. Although it was known that the decarboxylation of FDCA gradually occurred between 230 and 260°C, [17] the polymerization of FDCA and
aromatic diacetates had been previously carried out at 300° C. [14] The polymerizations of FDCA and DAB were carried out at 240° C to suppress the decarboxylation in DPE. Then, DPE was removed by vacuum distillation and the polymerization temperature was raised to 270° C to increase the molecular weight. Table 3-1 summarized the results of polymerization. Polyesters prepared from FDCA and 1,3-/1,4-DAB were described as F-PEs-χ. F-PEs-100 was obtained with good yield. In contrast, the yield of F-PEs-0 and F-PEs-50 were much lower than that of F-PEs-100. The sublimation occurred severely during the polymerization under vacuum. The sublimates were collected and analyzed by the FT-IR and $^1$H-NMR, and they contained unreacted FDCA predominantly as shown in Figure 3-1. The weight percent of the sublimate to FDCA in feed ($W_s$) was 70 and 61 wt% at the χ of 50 and 0 mol%, respectively. In addition, the oligomer prepared by the solution polymerization of FDCA and 1,3-DAB at 230° C for 6 h in DPE was

<table>
<thead>
<tr>
<th>Polymer code</th>
<th>χ (mol%)</th>
<th>Yield (%)</th>
<th>$W_s$ (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-PEs-100</td>
<td>100</td>
<td>71</td>
<td>5</td>
</tr>
<tr>
<td>F-PEs-50</td>
<td>50</td>
<td>8</td>
<td>70</td>
</tr>
<tr>
<td>F-PEs-0</td>
<td>0</td>
<td>18</td>
<td>61</td>
</tr>
</tbody>
</table>

*Polymerizations were carried out at 240° C for 6 h in DPE and 270° C for 3 h under vacuum after removal of DPE.

*Wight percent of sublimate after the polymerization to FDCA in feed
collected and the reduced viscosity of the oligomer was measured in acetone. The value of reduced viscosity was 0.09 dL g\(^{-1}\), suggested that the molecular weight did not increase by the solution polymerization. These resulted indicated that the FDCA did not react well with 1,3-DAB before the polymerization under vacuum. This might be owing to the large difference of reactivity between 1,3- and 1,4-DAB and the termination by the formation of cyclic oligomers. Therefore, the kinetics of the polymerization of

Figure 3-1. (a) FT-IR and (b) \(^1\)H-NMR spectrum of sublimates
FDCA and 1,3-/1,4-DAB in DPE were measured by acid-base titration of evolved acetic acid with aqueous sodium hydroxide and the oligomers were analyzed by MALDI-TOF mass.

As for the kinetics measurements, the reactions obeyed the second-order kinetics at the early stage of polymerization as shown in Figure 3-2 and the rate constants \( (k_2) \) were estimated from the slopes in Figure 3-2 as presented in Table 3-2 with activation energy \( (E_a) \). The \( k_2 \) value of the polymerization of FDCA and 1,3-DAB and that of FDCA and 1,4-DBA at 230\( ^\circ \)C were 3.82\( \times 10^{-4} \) and 3.75\( \times 10^{-4} \), respectively. In contrast, that of \( k_2 \) of the polymerization of FDCA and 1,4-DAB were higher than that of FDCA and 1,3-DAB.

![Figure 3-2](image.png)

**Figure 3-2.** Plots of number-average degree of polymerization (DPn) as a function of time in the initial stage of the polymerization of FDCA and 1,3-DAB or 1,4-DAB in DPE: Open marks are the polymerization of FDCA and 1,3-DAB, and solid marks are the polymerization of FDCA and 1,4-DAB. □ at 250\( ^\circ \)C, ■ at 245\( ^\circ \)C, △ and ▲ at 240\( ^\circ \)C, and ○ and ● at 230\( ^\circ \)C.
Table 3-2. Kinetic parameters of the polymerization of FDCA and DAB in DPE\(^a\)

<table>
<thead>
<tr>
<th>DAB</th>
<th>Temp.(^b) (°C)</th>
<th>(k_2)(^b) (L mol(^{-1}) min(^{-1}))</th>
<th>(E_a)(^c) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>230</td>
<td>3.82×10(^{-4})</td>
<td></td>
</tr>
<tr>
<td>1,3-DAB</td>
<td>240</td>
<td>1.43×10(^{-3})</td>
<td>2.61×10(^2)</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>4.23×10(^{-3})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>3.75×10(^{-4})</td>
<td></td>
</tr>
<tr>
<td>1,4-DAB</td>
<td>240</td>
<td>2.38×10(^{-3})</td>
<td>4.88×10(^2)</td>
</tr>
<tr>
<td></td>
<td>245</td>
<td>1.23×10(^{-2})</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Initial concentration of FDCA was 0.21 mol/L

\(^b\) Second-order rate constant

\(^c\) Activation energy calculated from Arrhenius plot

at higher than 240°C. Furthermore, number-average degree of polymerization (DPn) of oligomers prepared from FDCA and 1,3-DAB at 240°C for 6 h was estimated from \(k_2\), and it was 1.11 at most. The \(E_a\) for the polymerization of FDCA and 1,4-DAB was approximately 1.9 times higher than that of FDCA and 1,3-DAB. It is inferred from these results that the polymerizations did not proceed well in presence of 1,3-DAB in DPE due to the reactivity difference between 1,3-DAB and 1,4-DAB. According to the acidolysis reaction mechanism of carboxylic acid and aromatic acetate, \([18-20]\) the first reaction occurs by the nucleophilic attack of ether of carboxylic acid to the carbonyl carbon of the acetate as shown in Scheme 3-2. A tetrahedral intermediate is formed, which either reverts back to the starting materials or goes on by elimination of the
leaving group. The former is the more favorable step, but removal of acetic acid will derive the reaction toward completion at high temperature. Then, the generated phenol can attack either the acyl or the carbonyl group close to furan ring of the mixed anhydride. The former is a backward reaction step, while the latter leads to the formation of ester via a second tetrahedral intermediate. Nucleophilicity of phenol generated from 1,4-DAB is higher than that of 1,3-DAB due to the resonance effect.

It is known that the cyclic oligomers are often formed in polycondensation system of polyesters and polyamides [21]. Cyclic oligomers could be formed due to the kink-structure of FDCA and 1,3-DAB. The oligomers prepared by the solution polymerization of FDCA and DAB at the $\chi$ of 50 mol% at 230°C for 6 h in DPE were collected and analyzed by MALDI-TOF mass. The spectrum and the peak assignments were presented in Figure 3-3 and Table 3-3. The linear oligomers were mainly formed

\[
\begin{align*}
\text{Scheme 3-2. Reaction mechanism of carboxylic acid and aromatic acetate}
\end{align*}
\]
Table 3. Structural assignment of peaks in the MALDI-TOF mass spectrum of Figure 3-3

<table>
<thead>
<tr>
<th>Peak code</th>
<th>Structure</th>
<th>n</th>
<th>Mass (m/z)</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
<td></td>
<td>Calc.</td>
</tr>
<tr>
<td>A</td>
<td><img src="image" alt="Structure A" /></td>
<td>1</td>
<td>367.44</td>
</tr>
<tr>
<td>B</td>
<td><img src="image" alt="Structure B" /></td>
<td>1</td>
<td>463.47</td>
</tr>
<tr>
<td>C</td>
<td><img src="image" alt="Structure C" /></td>
<td>3</td>
<td>691.55</td>
</tr>
</tbody>
</table>

Figure 3-3 MALDI-TOF mass spectrum of the oligomer prepared from FDCA and DAB at the χ of 50 mol% at 230°C for 6 h in DPE.
and the cyclic oligomers were very slightly formed. Hence, the termination of polymerization due to the cyclization was negligible.

3-3-2 Bulk and solid state polymerizations

As mentioned above, the reactivity difference between 1,3-DAB and 1,4-DAB was identified. On the basis of kinetic measurements, the melt polymerizations of FDCA and DAB were carried out at 230°C at the initial stage of polymerization and then at 250°C to cause the transesterification efficiently. Then, the mixture was pulverized and the solid state polymerizations were applied at 270°C under reduced pressure. The polymerization of other dicarboxylic acid such as TPA, IPA and TDCA, and DAB were carried out in the same manner. The polymerizations proceeded at heterogeneous state until 0.5 h in all cases, and then the mixture melted gradually. The reaction mixture turned out to solidify completely until 3 h at the $\chi$ of 60 to 100 mol%. In contrast, the polymerization proceeded under very viscous molten state throughout the polymerization at the $\chi$ of less than 60 mol%. Although the sublimation was occurred very slightly in this method, the polymers were prepared with good yield. The $W_s$ was 8 wt% at the $\chi$ of 50 mol%, which was lower than solution polymerization. Since all PEss were insoluble to any organic solvents, the chemical structure of them was analyzed by FT-IR. The spectra of F-PEss were illustrated in Figure 3-4. As for F-PES-100, C=O stretching peaks of carboxylic acid and acetoxy group at 1697 and 1765 cm$^{-1}$
disappeared. O-H stretching peak of carboxylic acid at 3300 to 2450 cm\(^{-1}\) also did. C=O and C-O-C stretching peaks of ester were observed at 1745 and 1270 cm\(^{-1}\). This result revealed that F-PEss were prepared by the bulk and solid state polymerization. Furthermore, in the case of copolymerization, C=C stretching peaks were found both at 1502 cm\(^{-1}\) for \(p\)-phenylene ring and 1479 cm\(^{-1}\) for \(m\)-phenylene ring, and the ratio of the peak strength of \(p\)-phenylene ring to \(m\)-phenylene ring increased with the \(\chi\) value.
T-PEss, Th-PEss and I-PEss prepared from TPA, TDCA and IPA with DAB also prepared in the same procedure.

3-3-3 Characterization of PEss

Figure 3-5 showed the WAXS profiles of F-PEss. F-PEss at the $\chi$ of 100-20 mol% were crystalline and the crystallinity decreased with the decrease in $\chi$. As for the copolymerization, the diffraction peaks appeared newly at lower angle such as $2\theta = 14.8^\circ$ for F-PEs-50 and $2\theta = 14.0^\circ$ for F-PEs-20. It is conceivable that the packing of these F-PEss is loosened with the increase of 1,3-phenylene moiety. F-PEs-0 was amorphous. The melting and glass transition temperature could not be detected clearly by DSC measurements. The latent heats of phase-change seemed to be lower, and therefore the $T_{k\rightarrow s}$ was measured visually on a micro melting point apparatus to evaluate melting behavior instead of the DSC measurement. Thermal properties of F-PEss were characterized as summarized in Figure 3-6 with those of T-PEss and Th-PEss as comparison. F-PEs-100 and F-PEs-80 did not melt under 400°C. On the other hand, F-PEss melted at $\chi$ of 60-0 mol% and the $T_{k\rightarrow s}$ decreased with the decrease in $\chi$. The $T_{k\rightarrow s}$ of F-PEs-0 was 138°C and the lowest among F-PEss. The similar tendency was also observed for T-PEss and Th-PEss. The POM measurement was performed to evaluate liquid crystallinity and the micrographs of F-PEss were illustrated in Figure 3-7. F-PEs-60, F-PEs-40 and F-PEs-20 showed anisotropy at about $T_{k\rightarrow s}$, indicated that
F-PEss possessed nematic liquid crystalline in middle of the copolymerization ratio. The anisotropic phase turned out to be isotropic melts with elevating temperature. As for F-PEs-0, the anisotropic phase was not observed at all. The $T_{N\rightarrow I}$ was measured on a POM to determine the range of the anisotropic phase as also shown in Figure 3-6. The $T_{N\rightarrow I}$ of F-PEs-20 was 170°C and the temperature increased with $\chi$. Comparing F-PEs
with Th-PEs and T-PEs at the same of $\chi$, the $T_{k\rightarrow s}$ and $T_{N\rightarrow I}$ increased in following order: F-PEs $<$ Th-PEs $<$ T-PEs. I-PEss did not appear anisotropic phase at any $\chi$. It has been reported that 2,5-furandicarbonyl moiety was hard to play as mesogen itself and reduced the melting temperature due to the non-linear structure as well as 1,3-phenylene moiety. [22, 23] In contrast, 2,5-thiophenedicarbonyl moiety which is the homologue of heterocyclic ring worked as a mesogen. [24] The core angle of carbonyl-furan-carbonyl is approximately $133^\circ$ [22]. The core angle of 1,4-phenylene, 2,5-thiophenedicarbonyl and 1,3-phenylene moiety are $180^\circ$, $148^\circ$ and $120^\circ$, respectively. [24] It is conceivable that the core angle influences the formation of anisotropic phase and 2,5-disubstituted
Figure 3-7. Polarizing optical micrograph of (a) F-PEs-20 and (b) F-PEs-40 under cross polarization
furan ring has disadvantage to be a mesogen in term of the geometric feature. Although these data implied that the stability of anisotropic phase of F-PEss was lower than Th-PEss and T-PEss, 2,5-disubstituted furan ring possessed enough potential to form liquid crystalline phase. The temperatures of 10% weight loss ($T_{d10}$) in nitrogen atmosphere measured on a TGA of F-PEss were over 430°C and they showed excellent thermal stability comparable to common aromatic PEss.

Mechanical properties of undrawn film of F-PEs-20 prepared by melt-press were examined. The stress-strain curve of the F-PEs-20 film which had 370 μm of thickness was shown in Figure 3-8 with that of I-PEs-20 which had 340 μm of thickness for comparison. The tensile strength (σ) and elongation (ε) at break of the F-PEs-20 film were 26.0 MPa and 2.9%. The tensile modulus (E) was 1.2 GPa. Since I-PEs-20 films were 27.8 MPa of σ, 3.1 % of ε and 1.0 GPa of E, suggesting that F-PEs possessed good mechanical properties comparable to common aromatic PEss. Dynamic viscoelasticity was also measured on the dried F-PEs-20 film to evaluate relaxation behavior as shown in Figure 3-9 in the temperature range of -150 to 250°C. Although the initial storage modulus ($E'$) decreased slightly with temperature, it showed high value up to 140°C. The reduction of $E'$ started at 145°C which corresponding to $T_{k→s}$ of F-PEs-20. Then, $E'$ decreased drastically. With respect to tan δ, the magnitude of α-relaxation at 168°C was the largest among the relaxation. The β- and γ-relaxation were observed at 42°C and -55°C which might be derived from local motion of aromatic rings and carbonyl moiety.
Figure 3-8. Stress-strain curves of as prepared F-PEs-20 (solid line) and I-PEs-20 (dashed line) films: The thickness of F-PEs-20 and I-PEs-20 were 370 µm and 340 µm.

Figure 3-9. Viscoelastic behavior of as prepared F-PEs-20 film measured at 10 Hz
3-4 Conclusions

F-PEss were synthesized from bio-based FDCA with petroleum-based 1,3- and 1,4-DAB by the melt and solid state polymerization. The polymerization conditions were optimized by kinetics in solution polymerization. F-PEss at $\chi$ of less than 60 mol% showed meltability under decomposition temperature. When the value of $\chi$ was 20-60 mol%, they exhibited optical anisotropicity in melt phase, suggesting the thermotropic liquid crystallinity. Although the stability of anisotropic phase of F-PEss was lower than that of Th-PEss and T-PEss, F-PEss possessed enough potential to form thermotropic liquid crystals. The phase transition temperature of these PEss depended on the composition and it was tunable by the $\chi$ value. The film of F-PEs-20 possessed 1.2 GPa of the tensile modulus, 26.0 MPa and 2.9% of the strength and elongation at break, respectively. Polyesters based on FDCA possessed good thermal stability and mechanical properties comparable to common aromatic PEss.

3-5 References


Wiley-VCH, Chapter 8, p. 239.


CONCLUDING REMARKS

Commonly used high performance polymers had been prepared from petroleum-based aromatic monomers. From the viewpoint of petroleum consumption, preparation of them from bio-based materials which are renewable resources is of great importance to establish sustainable development society. Recently, poly(lactic acid) have been synthesized from bio-based material as an alternative to commodity polymers. However, few bio-based monomers have a potential for high performance polymers. Among them, 2,5-furandicarboxylic acid (FDCA) prepared from cellulose, glucose and fructose has been attracted attention as a bio-based aromatic dicarboxylic acid comparable or substitutable to commercial available aromatic dicarboxylic acid such as terephthalic acid and isophthalic acid. Although a plenty of types of polyesters, polyamides and others have been synthesized from FDCA and its related compounds by condensation polymerization, high performance polymers have hardly been synthesized from them. Further, the detailed properties of furan-ring containing polymers have not been clarified. Therefore, it is of importance to grasp a potential for high performance polymers of furan-ring containing polymers. In this thesis, aromatic poly(ether ketone)s and wholly aromatic polyesters which are known as representative high performance polymers were synthesized by the polycondensation of FDCA and the related compounds with petroleum-based monomers, and the properties were examined to clarify their potentiality as high performance polymers.
In Chapter 1, the Friedel-Crafts polymerizations of 2,5-furandicarboxyl dichloride (FDCC) and the aromatic ethers such as diphenyl ether (DPE) and 1,4-diphenoxobenzene (DPB) with Lewis acid such as aluminum chloride (AlCl₃), tin(+IV) chloride (SnCl₄) and zinc chloride (ZnCl₂) were carried out to prepare furan-ring containing aromatic poly(ether ketone)s (F-PEK). The polymerizations in 1,2-dichloroethane (DCE) and nitrobenzene (NB) which were common molecular solvents for the Friedel-Crafts polymerizations with SnCl₄ and ZnCl₂ did not proceed at all. The polymerizations in DCE and NB with AlCl₃ which possessed higher Lewis acidity than SnCl₄ and ZnCl₂ did not yield the high molecular weight F-PEKs due to the low swellability of precipitated physical gels among solvent, catalyst and the oligomers. In the Friedel-Crafts polymerization, the polymerizations usually gave the physical gel of the oligomer-AlCl₃ complex at the early stage of polymerization, and then polymerization underwent in the physical gels swollen by the solvents. The polymerizations were carried out in various 1-n-alkyl-3-methylimidazolium-based ionic liquids to form swollen gels. The polymerizations in 1-n-butyl-3-methylimidazolium chloride ([C₄mim]Cl)-AlCl₃ mixture afforded high molecular weight F-PEKs. The number average molecular weight of F-PEK prepared from FDCC and DPE was 7,200, and that from FDCC and DPB was 13,000. The obtained F-PEKs were mainly comprised of para-isomer to ether-linkage with the small amount of ortho-isomer. The gels formed in [C₄mim]Cl were more highly swollen than in DCE. It was revealed by
the WAXS measurement that the swollen gels of the oligomer-AlCl₃ complex were efficiently formed in [C₄mim]Cl. In addition, the rate constant of the model reaction of FDCC and anisole became higher in [C₄mim]Cl than that in DCE and NB. The obtained F-PEKs exhibited good thermal stability and chemical resistance comparable to common PEKs and they were crystalline thermoplastic polymers, possessing high glass transition temperature and low melting temperature.

Furthermore, the Friedel-Crafts polymerizations of 2,5-thiophenedicarbonyl dichloride, which was not bio-based monomer, and DPE were carried out in DCE and [C₄mim]Cl-AlCl₃ mixture from the viewpoint of polymer chemistry of heterocyclic ring containing PEKs. Although the polymerizations in DCE yielded low molecular weight PEK, that in [C₄mim]Cl-AlCl₃ mixture afforded the high molecular weight PEK as well as the polymerization of FDCC and aromatic ethers.

In Chapter 2, the aromatic nucleophilic substitution polymerizations of atomatic bisphenols and 2,5-bis(4-fluorobenzoyl)furan (BFBF) prepared from FDCC were carried out to synthesize molecular weight F-PEKs enough high to characterize for the estimation of the potential for high performance polymers with the comparison of common PEKs. At first, the model reaction of BFBF and p-methoxyphenol in presence of potassium carbonate (K₂CO₃) as a catalyst was carried out to clarify the reactivity of BFBF for the aromatic nucleophilic substitution reactions. Although the reactivity for the reaction of BFBF was lower than that of the homologue
1,4-bis(4-fluorobenzoyl)benzene, the model reaction formed the ether linkage with good conversion. Taking the results of reactivity into account, the polymerizations of BFBF and aromatic bisphenols in presence of K$_2$CO$_3$ were carried out in aprotic polar solvents. The polymerizations afforded F-PEKs with good yields. The longer polymerization time brought about the formation of insoluble parts in any solvents and the reduction of molecular weights. The obtained F-PEKs exhibited excellent thermal stability and chemical resistance comparable to common PEKs. F-PEK synthesized from BFBF and 4,4’-dihydroxydiphenyl ether became tough film by melt-press, and the tensile strength, elongation at break and tensile modulus of the film were 78.0 MPa, 6.2% and 1.2 GPa, respectively. It possessed good mechanical properties comparable to common high performance polymers. The thermal properties such as melting and glass transition temperature, solubility and crystallinity were tunable with the monomer structures of aromatic bisphenols.

In Chapter 3, wholly aromatic polyesters (F-PEss) were synthesized from FDCA with petroleum-based 1,3- and 1,4-diacetoxybenzene (DAB) by the melt and solid state polymerization with changing the molar ratio of 1,4-DAB in feed ($\chi$). The polymerization conditions were optimized by kinetics in solution polymerization. F-PEss at $\chi$ of more than 60 mol% did not melt under decomposition temperature. In contrast, F-PEss at $\chi$ of less than 60 mol% showed meltability under decomposition temperature. When the value of $\chi$ was 20-60 mol%, they exhibited optical anisotropicity
in melt phase, suggesting the thermotropic liquid crystallinity. The stability of anisotropic phase of F-PEss was compared to the homologue PEs prepared from terephthalic acid and 2,5-thiophenedicarboxylic acid. Although the stability of anisotropic phase of F-PEss was lower than that of 2,5-thiophenedicarboxylic acid-based and terephthalic acid-based PEss, F-PEss possessed enough potential to form thermotropic liquid crystals. The phase transition temperature of these PEss depended on the composition and it was tunable by the $\chi$ value. The film of F-PEs at $\chi$ of 20 mol% possessed 1.2 GPa of the tensile modulus, 26.0 MPa and 2.9% of the strength and elongation at break, respectively. Polyesters based on FDCA possessed good thermal stability and mechanical properties comparable to common aromatic PEss.

The present research could not only establish the preparation of the furan-ring containing polymers but also reveal that the obtained polymers in this work possessed enough potential for high performance polymers comparable to them. The Friedel-Crafts polymerizations in ionic liquid were a new approach to overcome a problem in polymer synthesis. Moreover, the properties of the polymers in this work were tunable with the structure in main chain.
LIST OF PUBLICATIONS

[1] Preparation of Poly(ether ketone)s Derived from 2,5-Furandicarboxylic Acid by Polymerization in Ionic Liquid
Kanetaka, Y, Yamazaki, S. and Kimura, K,

[2] Preparation of Poly(ether ketone)s Derived from 2,5-Furandicarboxylic Acid via Nucleophilic Aromatic Substitution Polymerization
Kanetaka, Y, Yamazaki, S. and Kimura, K,
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