Solid-state Synthesis of Fluorine-containing Poly(ether oxadiazole)

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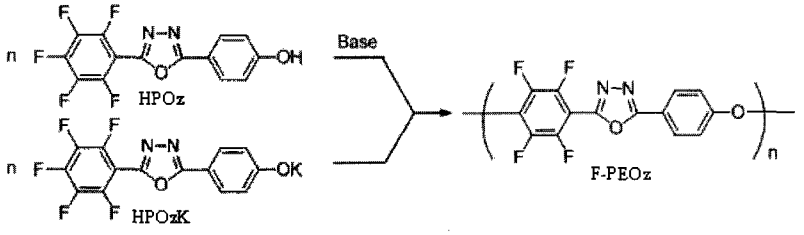
INTRODUCTION

Incorporation of fluorine atoms into polymer chains leads to polymers with increased solubility, thermal stability and glass transition temperature while also leading to decreased color, crystallinity, dielectric constant and moisture absorption. Owing these advantages, many types of fluorine-containing aromatic polymers have been synthesized as high-performance materials for optical and microelectronics devices, aerospace application, gas separation membranes and so on. [1-4] Fluorine-containing aromatic polymers such as poly(arylene ether ketone), poly(arylene ether sulfone) and so on, have been synthesized, [5-9] and the demand for these fluorine-containing aromatic polymers increases.

Poly(arylene 1,3,4-oxadiazole)s had been developed as a class of thermally stable polymers. [10-12] Due to their excellent heat and solvent resistance, they have been used for high performance materials. Recently, their optical and electronic properties have been receiving attention to create novel devices [13-17] as well as high performance materials. [18-24] Since they have limited solubility in common organic solvents, they are generally processed from the soluble polyhydrazide precursors. Fluorine-containing poly(arylene ether 1,3,4-oxadiazole)s were prepared by the nucloephilic aromatic substitution reaction of 2,5-bis(2,3,4,5,6-pentafluorophenyl)-1,3,4-oxadiazole and various bisphenols to improve their solubility by the incorporation of 2,3,5,6-tetrafluoro-1,4-phenylene moiety. [25, 26] These fluorine-containing poly(arylene ether 1,3,4-oxadiazole)s exhibited high Tg and good thermal stability beside excellent solubility. Although polymerizations by the nucloephilic aromatic substitution reaction are usually carried out at 180 – 200°C, they could be synthesized at lower temperature of 80°C because of the quite high reactivity of 2,5-bis(2,3,4,5,6-pentafluorophenyl)-1,3,4-oxadiazole.

Thermally induced solid-state polymerization had been studied and many types of polymerizations had been developed so far. [27] Solid-state polymerization has been recently paid much attention from the viewpoint of environmentally benign polymerization. Aliphatic polyesters such as polyglycolide, [28, 29] polylactide [30] had been synthesized. Aromatic polyesters such as poly(hydroxymethylbenzoic acid)s were also prepared by solid-state polymerization from sodium and potassium 4- or 3-halogenomethylbenzoate. [31, 32] These studies strongly suggest that if the monomer possesses enough high reactivity under its decomposition temperature, the nucleophilic aromatic substitution reaction occurs in solid-state. On the basis of these previous studies, it can be expected that the fluorine-containing poly(ether 1,3,4-oxadiazole) is synthesized by thermally induced polymerization in solid-state.

2-(4-Hydroxyphenyl)-5-pentafluorophenyl-1,3,4-oxadiazole (HPOz) is a monomer of F-PEOz. This



Scheme 1. Synthesis of F-PEOz

self-polymerizable monomer is desirable for the solid-state polymerization because of the stoichiometric condition. Hence, this paper reports the synthesis of F-PEOz by the solid-state polymerization of HPOz as shown in Scheme 1.

EXPERIMENTAL

Materials

2,3,4,5,6-Pentafluorobenzoic acid was a gift of Nippon Shokubai Co. Ltd. 4-Hydroxybenzhydrazide, thionyl chloride, *N,N*-dimethylacetamide (DMAc) and 1-methy-2-pyrrolidinone (NMP) were purchased from Aldrich Co. Ltd. 4-Hydroxybenzhydrazide and thionyl chloride were used as received. DMAc and NMP were purified by distillation under reduced pressure over calcium hydride and stored over 4A molecular sieves.

Characterization

NMR spectra were recorded on a JEOL AL300 SC-NMR at 300 MHz (^{1}H) and 298 MHz (^{19}F). 4,4'-Difluorobenzophenone was used as an internal standard for ^{19}F-NMR measurements. FT-IR spectra were measured on a JASCO FT/IR-410 spectrometer. Morphology of products was observed on a HITACHI S-3500N scanning electron microscope (SEM). Samples were dried, sputtered with platinum-palladium and observed at 20kV. Wide angle X-ray scattering (WAXS) pattern was measured on a Rigaku Gaiger Flex with nickel-filtered CuKα radiation (35 kV, 20 mA). Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC 7 at a scanning rate of $10^{\circ}C \cdot min^{-1}$ in nitrogen atmosphere. Temperature and heat flow were calibrated using indium and zinc as the standards. Thermal stability was measured by thermogravimetric analysis on a Perkin-Elmer TGA 7 at a heating rate of $10^{\circ}C \cdot min^{-1}$ in nitrogen atmosphere. Reduced viscosity (sp/C) was measured with an Ostwald-Fenske viscometer in DMAc at a concentration of 0.5 $dL \cdot g^{-1}$ at 25°C. Water contact angle was measured on a Contact angle meter CA-D, Kyowa Kaimen Co. Ltd. A film was prepared on a glass plate by casting the polymer solution in DMAc, and the contact angle was measured on a film surface on the glass plate, because the film was slightly brittle.

Synthesis of HPOz

Into a solution of 4-hydroxybenzhydrazide (7.26g, 47.7mmol) in 30 ml of NMP, a solution of 2,3,4,5,6-pentafluorobenzoyl chrolide (11.00g, 47.7mmol), which was synthesized from 2,3,4,5,6-pentafluorobenzoic acid and thionyl chloride according to the previous procedure,[5] in 44 mL of NMP was slowly added at –10°C and the mixture was stirred at –10°C for 12 h. The mixture was poured into water and white solids were collected by filtration. The obtained white solids were dried under vacuum at 30°C for 12 h. Recrystallization from a mixture of methanol and water gave 1-(4-hydroxyphenyl)-4-pentafluorophenylhydrazide (HPH) with the yield of 73.0% (12.1g). A solution of HPH (3.98g, 11.5mmol), 0.4 mL of pyridine and 20 mL of thionyl chloride was refluxed for 2 h. Excess of thionyl chloride was stripped off under vacuum, and the obtained solids were washed with water and dried under vacuum at 30°C for 12 h. Recrystallization from methanol gave white crystals of HPOz with the yield of 98% (3.7g). Tm: 248°C. IR(KBr, cm^{-1}): 3060-2630 (phenolic OH), 2939 (aromatic C-H), 1247 (aromatic -C-O-C-), 1654 (1,3,4-oxadiazole C=N), 996 (1,3,4-oxadiazole -C-O-C-). ^{1}H-NMR(CD_3OD) δ(ppm): 10.46 (s, OH, 1H), 7.91 (d, aromatic, 2H), 6.99 (d, aromatic, 2H). ^{19}F-NMR(DMSO-*d6*) δ(ppm): -132.8(aromatic, 2F), -144.7(aromatic, 1F), -156.6(aromatic, 2F). Anal. Calcs. for $C_{14}H_5O_2N_2F_5$: C, 51.23; H, 1.53; N, 8.53. Found: C, 50.99; H, 1.43; N, 8.32.

Solution polymerization of HPOz

Into a 10 ml flask equipped with a Dean-Stark trap, a condenser, a magnet stirrer and nitrogen inlet and outlet tubes were placed HPOz (0.10 g, 0.30 mmol), potassium carbonate (0.042g, 0.15 mmol), 0.4ml of NMP and 2 mL of toluene. The mixture was refluxed for 3 h with eliminating by-produced water by azeotropic distillation and then toluene was distilled over. The solution was stirred for 20 h. The reaction mixture was allowed to cool to 25°C and poured into water containing 1% acetic acid under vigorous stirring. The precipitated polymers were collected by filtration, washed twice with water and then dried at 50°C under vacuum.

Solution polymerization of HPOz potassium salt (HPOzK)

Into a round flask equipped with gas inlet and out let tubes, a magnetic stirrer and a thermometer, were placed potassium hydroxide (0.061g, 0.91 mmol) and dried methanol (7 mL). HPOz (0.30g, 0.91 mmol) was added to this solution and then the mixture was stirred at 25°C for 30 min. After evaporating methanol, HPOzK was dried under vacuum at 30°C for 6 h. NMP (1.2 mL) was added into this HPOzK and the mixture was heated up to 150°C with stirring. The mixture was polymerized at 150°C for 10 h. After being allowed to cool at 25°C, the mixture was poured into water containing 1% acetic acid under vigorous stirring. Precipitated polymers were collected by filtration, washed with water and methanol, and then dried at 50°C under vacuum. The polymers were obtained with the yield of 96% (0.27g). Polymerizations in solution under other conditions were also carried out by the similar manner.

Solid-state polymerization

HPOzK was placed in a round flask equipped with gas inlet and outlet tubes. They were heated at 180°C in N_2 for 1 h. After being allowed to cool at 25°C, the solids were put into water containing 1% acetic acid under vigorous stirring. Precipitated polymers were collected by filtration, washed with water and methanol, and then dried at 50°C under vacuum. The polymers were obtained with the yield of 84% (0.24g). Tg: 246°C. Anal. Calcs. for $C_{14}H_5O_2N_2F_5$: C, 54.56; H, 1.31; N, 9.09. Found: C, 50.31; H, 1.79; N, 8.04. IR(KBr)(cm^{-1}): 2918 (aromatic C-H), 1229 (aromatic -C-O-C-), 1654 (1,3,4-oxadiazole C=N), 993 (1,3,4-oxadiazole -C-O-C-). Polymerizations in solid-state under other conditions were also carried out by the similar procedure.

RESULTS AND DISCUSSION

HPOz possesses the electron-withdrawing 1,3,4-oxadiazole ring directly connected to 2,3,4,5,6-pentafluorophenyl moiety, and therefore three aromatic carbons of one *para* position and two *ortho* positions to 1,3,4-oxadiazole ring might be more reactive toward the nucleophilic attack by a phenoxide moiety in itself. The activating 1,3,4-oxadiazole ring can also accept a negative charge lowering the activation energy for the displacement through a Meisenheimer complex. ^{19}F-NMR spectroscopy can be used to probe the π-electron density at the actual site and it is a sensitive tool in regards to the nucleophilic aromatic substitution. [25-27] ^{19}F chemical shift is corresponding to the π-electron density and the fluorine shifting lower field is more reactive for nucleophilic substitution due to higher electrophilicity. Chemical shifts of fluorine atoms attached to the phenyl group at *para* and *ortho* positions to 1,3,4-oxadiazole were –144.7 and –132.8 ppm, respectively. This result suggests that π-electron density at the *ortho* carbons is lower than the *para* carbon, and the *ortho* carbons possess higher reactivity than the *para* carbon in HPOz. The optimization of the polymerization condition is necessary to prevent the reaction at *ortho* positions leading to cross-linking for preparation of the

soluble F-PEOz.

Solution polymerization

Nucleophilic aromatic substitution polymerizations are generally carried out in aprotic polar solvents in the presence of bases. First, polymerizations were carried out in NMP at a concentration of 25 %. Results of the solution polymerization are presented in Table 1. Potassium carbonate was used to convert the phenol moiety into the more reactive anion. Toluene was used during the initial stages of the polymerizations to remove water generated by phenoxide formation as toluene azeotrope. Cross-linking reaction occurred even at 80°C and polymers became totally insoluble into NMP after 15 min (run no. 1). When toluene was entirely removed from the mixture, temperature was raised over 120°C, which was higher than the polymerization temperature. This high temperature might cause the cross-linking reaction. In order to avoid the cross-linking reaction at high temperature, HPOzK, which was prepared from HPOz and potassium hydroxide prior to the polymerization, was used as a monomer. The soluble polymers were obtained at 80-120°C for 20 h. The usefulness of solution viscosity has been generally recognized as a measure of polymer molecular weight. Solution viscosity is basically a measure of the size or extension in space of polymer molecules and it is empirically related to molecular weight. The ηsp/C is used as a measure of polymer molecular weight in this study. The values of ηsp/C were in the range of 0.11-0.15 $dL \cdot g^{-1}$. The ηsp/C of the polymers prepared at 120°C for 30 h was 0.12 $dL \cdot g^{-1}$ (run no. 5) and it did not increase with time. The obtained polymers possess low molecular weight. Insoluble polymer was formed quantitatively at 150°C (run no. 6), and it was formed only for 1 h at 180°C (run no. 7). The soluble polymers were not obtained at all at higher temperature than 150°C.

Table 1. Results of solution polymerization

Run no.	Polymerization condition [a]				Yield (%)	ηsp/C [b] ($dL \cdot g^{-1}$)	Insoluble part [c] (wt%)
	Monomer	Base	Temp. (°C)	Time (h)			
1	HPOz	K_2CO_3	80	0.25	75	-	100
2	HPOzK	-	80	20	89	0.13	0
3	HPOzK	-	100	20	88	0.15	0
4	HPOzK	-	120	20	91	0.11	0
5	HPOzK	-	120	30	84	0.12	0
6	HPOzK	-	150	10	96	-	100
7	HPOzK	-	180	1	71	-	100

[a] Polymerizations were carried out in NMP at a concentration of 25%. [b] ηsp/C was measured in DMAc at a concentration of $0.5 g \cdot dL^{-1}$ and 25°C. [c] Insoluble part in NMP.

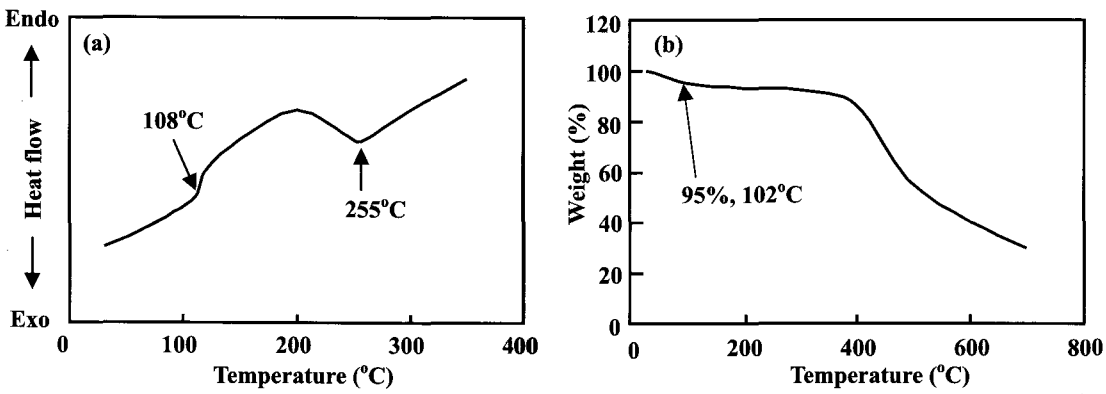


Figure 1. DSC (a) and TGA (b) thermogram of HPOzK measured at a scanning rate of $10°C \cdot min^{-1}$

Solid-state polymerization

It was quite difficult to prepare the soluble F-PEOz by the solution polymerization due to the cross-linking reaction. If the mobility of the molecules is restricted during polymerization, it is expected that the cross-linking reaction caused by the reaction at not only *para* but *ortho* positions, as discussed above, is slightly inhibited by the effect of steric hindrance. Thermal behaviors of HPOzK were measured on a DSC and a TGA as shown in Figure 1. A broad endothermic peak was observed from 108-255°C on heating in a DSC profile, which was not contributed to a melting behavior. Liquefaction was not observed, and therefore certain endothermic reaction might occur in solid-state. In a TGA profile, 5% weight loss was observed up to 102°C, whereas no weight loss was recorded from 110 to 380°C. On the basis of these results, an endothermic reaction recorded on a DSC is not a decomposition reaction, and it is likely the polymerization. Based on these results, polymerizations of HPOzK were carried out without solvents. Results of the solid-state polymerization are presented in Table 2. Polymerization at 120°C for 20 h gave soluble F-PEOz with the yield of 47% and the ηsp/C of 0.22 dL·g^{-1} (run no. 8). The molecular weight was higher than that prepared at 120°C for 20 h in NMP. Although the yield increased by the polymerization for 30 h, the ηsp/C was almost constant. The polymerization at 150°C for 10 h gave soluble F-PEOz with the yield of 75% and the ηsp/C of 0.27 dL·g^{-1} (run no. 10). Although the ηsp/C of polymers soluble in NMP increased to 0.74 dL·g^{-1}, the polymers obtained at 150°C for 20 h contained 40% insoluble part (run no. 11). The polymerization at 180°C for 1 h gave soluble F-PEOz with the yield of 84% and the ηsp/C of 0.66 dL·g^{-1} (run no. 12). Chemical structure of the F-PEOz obtained in run no. 12 was analyzed by ^{1}H, ^{19}F-NMR and IR spectroscopy. The NMR and IR spectra were shown in Figures 2 and 3, respectively. In ^{1}H-NMR spectrum of F-PEOz prepared for 1 h, two broad peaks were detected at δ of 7.9 and 7.3 ppm corresponding to aromatic protons at *ortho* and *meta* position to a 1,3,4-oxadiazole ring. The peak of phenolic OH in HPOz was not observed. In the ^{19}F-NMR spectrum, two large peaks were detected at δ of -132.5 and –149.1 ppm corresponding to aromatic fluorine atoms at *ortho* and *meta* position to a 1,3,4-oxadiazole ring. However, five small peaks were observ

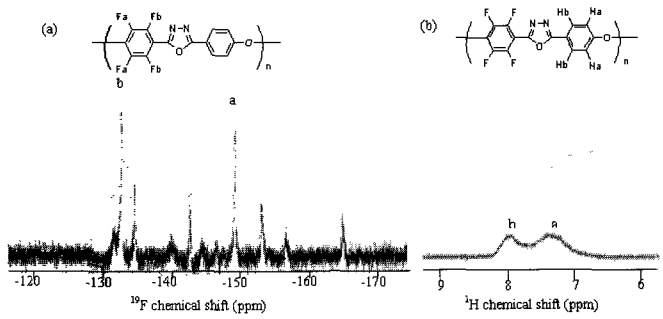


Figure 2. ^{19}F (a) and ^{1}H-NMR (b) spectra of F-PEOz prepared in solid-state at 180°C for 1 h (run no. 12). Spectra were measured in DMSO-*d6*.

Table 2. Res

Ru n no.	Polym cor Temp. (°C
8	120
9	120
10	150
11	150
12	180
13	180

[a] ηsp/C was mea and 25°C. [b] Inso in NMP.

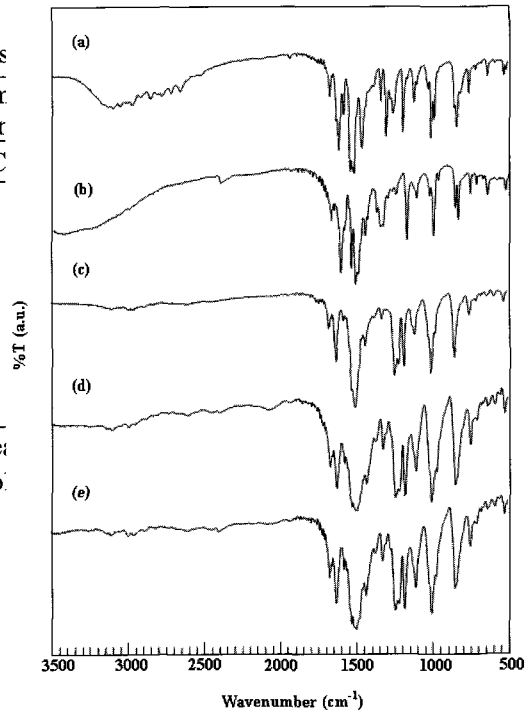


Figure 3. IR spectra of (a)HPOz, (b)HPOzK, F-PEOz prepared in solid-state at 180°C for (c) 0.5 h, (d) 1

ed at δ of –134.4, -142.5, -152.9, -156.4 and –164.8 ppm. The appearance of these peaks suggests that the substitution reaction also occurred at *ortho* positions and the polymer contains branched structures. This branched structure makes the peaks of aromatic protons broader. In the IR spectrum of F-PEOz prepared for 1 h, characteristic bands were detected at 1229 cm^{-1} (aromatic -C-O-C-), 1654 cm^{-1} (1,3,4-oxadiazole C=N) and 993 cm^{-1} (1,3,4-oxadiazole -C-O-C-). The broad peak at 3060-2630 cm^{-1} corresponding to phenolic OH of HPOz disappeared entirely after the polymerization. These spectra show that the nucleophilic aromatic substitution was occurred to form the ether linkage mainly at the carbons *para* to a 1,3,4-oxadiazole ring in HPOz. However, the reaction at the carbons *ortho* to a 1,3,4-oxadiazole ring could not be prevented completely and the resulting F-PEOz contained branched structures.

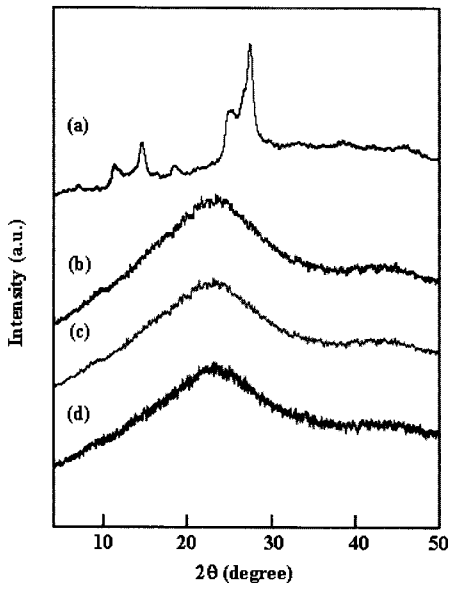


Figure 5. WAXS intensity profiles of (a) HPOzK, F-PEOz prepared in solid-state at 180°C for (b) 0.5 h, (c) 1 h (run no. 12) and (d) 3 h.

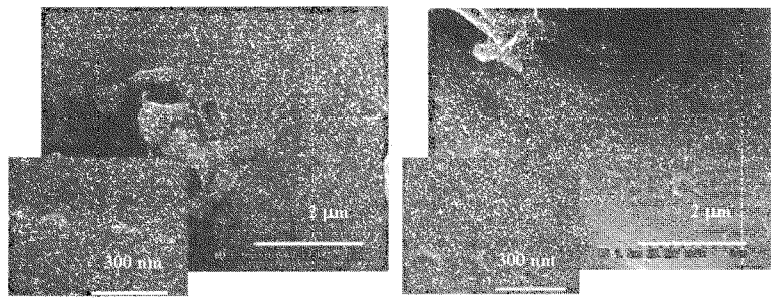


Figure 6. Morphology of surface of F-PEOz prepared in solid-state at 180°C for 1 h (a) before and (b) after washing (run no. 12).

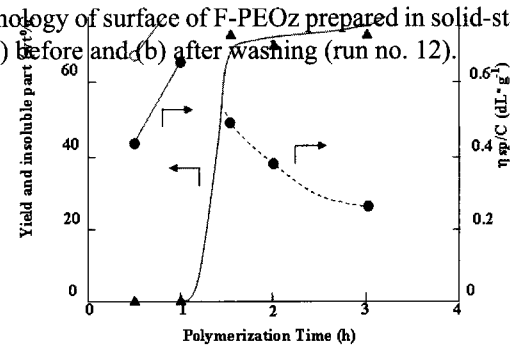


Figure 4. Plots of yield (○), insoluble part (▲) and ηsp/C (●) of F-PEOz as a function of polymerization time. Polymerizations were carried out in solid-state at 180°C. The values of ηsp/C after 1.5 h were those of soluble part.

HPOzK was yellow powders. The powders changed to orange, white and pale gray during the polymerization. The yield, the ηsp/C of the part soluble in NMP and the content of insoluble part were examined in the course of the polymerization of HPOzK at 180°C. The results were plotted as a function of time as shown in Figure 4. The yield increased with time and it became constant at 90% until 1.5 h. The ηsp/C also increased until 1 h. The polymer prepared for 1 h was entirely dissolved in NMP, but over 70% of the polymers became insoluble after 1.5 h. The cross-linking reaction rapidly took place from 1 to 1.5 h to form insoluble polymers. The ηsp/C of the soluble parts decreased with time after 1.5 h and all of the polymers became insoluble after 4 h. Change in IR spectrum was presented in Figure 3. The spectrum of F-PEOz prepared for 0.5 h is basically identical with that for 1 h. However, the bands from 1550 to 1400 cm^{-1}, which are the stretching of aromatic ring, became broader with time. This broadening is caused by the cross-linking reaction. WAXS profiles were shown in Figure 5. HPOzK has a reflection peaks at 2θ of 11.7, 14.9, 25.7, 27.0 and 27.8°, and they were crystalline. After 0.5 h, the reflection peaks of HPOzK disappeared and broad halo contributed from amorphous region was only visible from 2θ of 10 to 40°. The solids lost the crystallinity and the polymerization continued to proceed in amorphous phase. This polymerization did not take place topochemically. Change in the surface morphology of F-PEOz was

observed before and after washing with water. As shown in Figure 6, many small particles of which the size was ca. 50 nm were clearly observed on the surface of polymers before washing (as polymerized). However, they were disappeared after washing with water and many craters were observed on the surface, of which the size was approximately equal to the size of the particles. The potassium fluoride salts produced by the polymerization seem to precipitate as fine particles within the polymer matrix. They could be removed by washing with water, so that porous polymer surface remained. It has been reported that the high lattice energy of the alkali halide was a strong driving force for nucleophilic substitution to form poly(hydroxymethylbenzoic acid).[29] The similarity of this polymerization reaction to the solid-state polymerization of HPOzK suggests that the formation of potassium fluoride is likely a driving force of polymerization.

Properties of F-PEOz

Quantitative solubility of the F-PEOz was determined in excess of solvents at 25°C. F-PEOz was dissolved into polar aprotic solvents such as DMAc and NMP, whereas insoluble into toluene, acetone and THF. The incorporation of 2,3,5,6-tetrafluoro-1,4-phenylene moiety into the polymer structures enhanced the solubility due to the lower interaction between polymer chains. Glass transition temperature (Tg) of F-PEOz was 246°C and F-PEOz did not exhibit any endothermic events (e.g., melting behavior). As discussed with WAXS, F-PEOz was an amorphous polymer. Temperature of 10% weight loss in nitrogen atmosphere evaluated by TGA was 405°C. The char yield at 600°C in nitrogen atmosphere was 46%. The temperature of 10% weight loss of HPOzK was recorded at 390°C and its char yield at 600°C was 40% as shown in Figure 1. Thermal stability of F-PEOz is slightly higher than that of HPOzK which is a monomer. This fact implies that the solid-state polymerization occurred during the measurement of DSC. F-PEOz possessed good thermal stability. Water contact angle was measured on the surfaces of the film. The contact angle of F-PEOz film was 93.9° and the F-PEOz was hydrophobic due to the existence of fluorine atoms.

CONCLUSIONS

Although only low molecular weight or cross-linked F-PEOz was obtained by the solution polymerization with base, fully soluble F-PEOz was successfully synthesized by the solid-state polymerization of HPOzK at 180°C for 1 h with the yield and the ηsp/C of 84% and 0.66 $dL \cdot g^{-1}$, respectively. The obtained polymer was mainly *para*-connected structure but *ortho* positions also reacted, and it was a branched structure. The longer polymerization time gave insoluble polymers due to the cross-linked structure. From the WAXS measurements, the solid-state polymerization did not take place topochemically, and it occurred in amorphous state. The cross-linking reaction leading to the formation of insoluble polymer was inhibited by the solid-state polymerization. The obtained F-PEAs showed excellent solubility and exhibited high Tg of 246°C. They showed good thermal stability and hydrophobicity due to the incorporation of 2,3,5,6-tetrafluoro-1,4-phenylene moiety.

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