

Solid-state polymerization and characterization of a copolyamide based on adipic acid, 1,4-butanediamine, and 2,5-furandicarboxylic acid

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ABSTRACT: 2,5-Furandicarboxylic acid (FDCA) is a promising biobased alternative material to terephthalic acid. In this study, three types of poly(butylene adipamide) (PA-4,6) containing 10, 20, and 30 mol % of poly(butylene-2,5-furandicarboxylamide) (PA-4,F) were synthesized through consecutive prepolymerization and solid-state polymerization (SSP). The incorporation of a 10 mol % PA-4,F component into PA-4,6 resulted in slight increases in the intrinsic viscosity (IV) and glass-transition temperature (T_g) after 12 h of SSP at 220 °C. When the SSP temperature and reaction time increased, IV increased proportionally. The highest IV value of 0.75 was obtained by 48 h of SSP at 240 °C, whereas increases in the PA-4,F content to 20 and 30 mol % gave rise to decreases in IV, T_g , and melting temperature; this interrupted the increase in SSP temperature. The thermal decomposition temperature of the PA-4,F-incorporated polyamide was lower than that with PA-4,6 because of the lower thermal stability of the FDCA component. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43391.

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INTRODUCTION

Currently, most polymers are produced from petroleum-based materials. Concerns over the exhaustion of oil have led to need for alternative materials to petroleum-based polymer. Biomass-based polymers have been considered the most promising alternative, and a number of studies and development are underway in many areas of the world. Biopolyethylene produced from bio-ethanol,¹ polylactide,^{2,3} and triglyceride-based polymers⁴ are typical examples.

Polyamide (PA), generally known as nylon, can be synthesized from the amidation of diamines and diacids. Commercially, poly(hexamethylene adipamide) synthesized from 1,6-hexanediamine and adipic acid (AA) and polycaprolactam synthesized from ϵ -caprolactam have been used for general purposes. For decades, the synthesis of PA from short-chain monomers or

aromatic monomers has been studied to enhance the heat resistance of commercial PA. For example, Gaymans *et al.*⁵ reported that poly(butylene adipamide) (PA-4,6) and poly(butylene terephthalamide) (PA-4,T) synthesized from 1,4-butanediamine (BDA) and terephthalic acid (TPA) had higher melting temperatures (T_m 's) compared with poly(hexamethylene adipamide).

Numerous researchers have made efforts to obtain these monomers of PA from biomass, and remarkable advances have been achieved with respect to the synthesis of BDA,⁶ 1,5-pentanediamine,⁷ AA,⁸ and succinic acid.⁹

2,5-Furandicarboxylic acid (FDCA) is a biobased diacid synthesized from hexose.¹⁰ Because of its structure, which is analogous to that of TPA, FDCA has received attention as a substitute for TPA in the polymer industry. Several researchers reported that the FDCA–ethylene glycol-based polyester poly(ethylene 2,5-

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furandicarboxylate) has properties comparable to those of poly(ethylene terephthalate).^{11,12} As a result, the Coca-Cola Co. is known to be preparing the commercialization of poly(ethylene 2,5-furandicarboxylate).¹³ In addition, the synthesis of polyester from FDCA and various diols other than ethylene glycol has been studied, and promising results have been reported.^{12,14,15}

Accordingly, since the 1960s, the synthesis of PA from FDCA has been also examined. A few pioneering papers have reported the synthesis of PA from FDCA and aliphatic diamine,¹⁶ but the early investigations did not pursue the details related to the polymer properties. Later, Grosshardt *et al.*¹⁷ synthesized various kinds of PA by reacting FDCA with the alkane diamines of C₆–C₁₂. The PA synthesized from FDCA and 1,6-hexanediamine with the catalyst butyltin dihydroxide was reported to have a weight-average molecular weight (M_w) of 13,500 g/mol when polycondensation was conducted at 230 °C for 5 h under 100 Pa.

Aromatic PAs have been formulated by the polycondensation of FDCA and aromatic diamines, including 1,4-phenylenediamine and methylenedianiline.^{18,19} When the reactions were conducted under stoichiometric conditions in 1-methyl-2-pyrrolidinone (NMP)/pyridine in the presence of triphenyl phosphite, calcium, and lithium chloride at 90 °C for 20 h,¹⁹ FDCA-based PAs having a 0.55–1.33 dL/g inherent viscosity, depending on the kind of aromatic diamine, were synthesized.

Recently, Yutaka *et al.*²⁰ published results on polycondensation between FDCA and 1,3-propane diamine. At reaction temperatures in the range 220–240 °C, they reported the formation of poly(propylene-2,5-furandicarbonamide) having a M_w of 3200 and a glass-transition temperature (T_g) of 150 °C. They also undertook interfacial polymerization with 1,3-propanediamine and an acyl chloride derivative of FDCA to synthesize PA with M_w values in the range 30,000–50,000 g/mol.²⁰ Although this interfacial polymerization process appeared to be quite successful in how it increased the M_w of furan-based PA, the use of toxic SO₂Cl₂ for the introduction of the reactive acyl group onto FDCA, the use of NaOH for the neutralization of the byproduct HCl, and the large amount of water consumed during the polymerization step devalued the advantages of the use of a biobased PA monomer.

Solid-state polymerization (SSP) is another means of increasing the M_w of PA. Because this process is conducted in the absence of a solvent, SSP is known as an environmentally benign polymerization process. Therefore, numerous polymers have been synthesized by SSP, including PA,²¹ polyester,^{22–27} and polycarbonate.^{28–32}

Previously, we studied the synthesis of a copolyamide consisting of PA-4,6 and PA-4,T using SSP.³³ We found that with an increase in the terephthalate component, the T_g , T_m , and thermal decomposition temperature (T_d) values of the resulting PAs increased, whereas the SSP rate decreased.

In this study, to verify the feasibility of SSP to synthesize a biobased PA containing FDCA and to investigate the effects of the process parameters on the polymerization, a copolymer of poly-

(butylene-2,5-furandicarboxylamide) (PA-4,F) and PA-4,6 was synthesized, and its thermal properties, including T_g , T_m , and T_d , and intrinsic viscosity (IV), were measured. The presence of a furan group on the polymer was verified with UV and ¹H-NMR spectroscopy.

EXPERIMENTAL

Materials

All reagents except FDCA were purchased from Sigma-Aldrich Chemical Co. FDCA was obtained from Haihang Industry Co., Ltd. (China). FDCA was purified with DMSO/water. Water was ultrafiltered with a water purification system (Cascade RO-Water Purification System, Pall Corp.) and used as a solvent in salt preparation, prepolymerization, and SSP. Nitrogen (>99.8%, Shinyang Sanso Co., Korea) purified through an oxygen trap (model 20601, Restek) was used as a sweep gas during polymerization. Concentrated sulfuric acid (>98.0%, Daejung Chemicals and Metals, Korea) was used as a solvent for the measurement of IV.

Preparation of the Salts

The salt of BDA and AA (4,6 salt) was prepared with the following procedure: 88.1 g of BDA (1.0 mol) was dissolved in 500 mL of methanol with vigorous stirring at 25 °C. Next, 146.1 g of AA (1.0 mol) in 500 mL of methanol was slowly added to the solution of BDA in methanol and stirred for 1 h. Precipitation was observed as soon as AA was introduced into the solution, and the total reaction was generally finished in 1 h. The mixture was cooled to 25 °C to precipitate the 4,6 salt. The obtained salt was filtered off, washed with cold methanol, and dried at 50 °C in a vacuum oven for 48 h. The salt of BDA and FDCA (4,F salt) was prepared in a similar manner to that used in the synthesis of 4,6 salt.

Prepolymerization

The synthesis of the prepolymer was carried out with the same apparatus described in the previous study.³³ Mixtures of the 4,6 and 4,F salt with different molar ratios (total weight 400 g) were each dissolved in 200 g of purified water and introduced into a 1.5-L high pressure reactor equipped with a magnetically driven stirrer. Next, the reactor was closed and purged with nitrogen for about 30 min to remove all of the oxygen inside. The reaction temperature was increased to 170 °C in 1 h, maintained for 1 h, then increased to 220 °C for 1 h, and maintained at that temperature for 6 h. During the reaction, the reactor pressure was controlled at 0.3 MPa with the back-pressure regulator. After the reaction, the prepolymer was isolated, ground into a certain particle size, and used in the solid-state polymerization process. Prepolymers prepared from mixtures of 4,6 salt and 4,F salt with molar ratios of 9:1, 8:2, and 7:3 were denoted as PAP-F-10, PAP-F-20, and PAP-F-30, respectively. Prepolymers synthesized with a single salt, 4,6 salt and 4,F salt, were marked as PAP-4,6 and PAP-F-100, respectively.

SSP

SSP was also conducted with the same equipment used in a previous study.³³ The reactor was charged with 1.5 g of the prepared prepolymer and put inside the forced-convection oven. The reactor was purged with nitrogen at a flow rate of

Table I. Properties of the Prepolymers Synthesized from the Mixture of 4,6 Salt and 4,F Salt

Prepolymer	4,6 Salt/4,F salt molar ratio	IV (dL/g)	T_g (°C)	T_m (°C)	ΔH_f (J/g)
PAP-4,6	100:0	0.21	56	281	108
PAP-F-10	90:10	0.40	65	271	63
PAP-F-20	80:20	0.20	52	267	54
PAP-F-30	70:30	0.13	48	246	38
PAP-F-100	0:100	0.07	—	—	—

The conditions were 400 g of salt, 200 g of water, 170°C for 1 h, 220°C for 6 h, and 0.3 MPa.

2000 mL/min for 5 min, and the temperature was increased to 120 °C over 10 min. When the reactor temperature reached 120 °C, the mixture of steam and nitrogen was introduced into the reactor at a ratio of N₂ to water of 2:1. After 1 min, the reactor temperature was increased to a predetermined temperature and kept at that temperature for a predetermined time. When SSP was completed under the desired reaction conditions, the reactor was rapidly cooled to 120 °C with nitrogen purging to remove the residual water. Finally, the reactor was cooled to ambient temperature, and the product was recovered and analyzed. SSP polymers synthesized from PAP-4,6, PAP-F-10, PAP-F-20, and PAP-F-30 were marked as PA-4,6, PA-F-10, PA-F-20, and PA-F-30, respectively.

Characterization

For the comparison of molecular weight, the IV was measured. The polymer was dissolved in concentrated sulfuric acid, and its IV was determined with an Ubbelohde viscometer equipped with an automatic data acquisition system (model Visco System AVS 370) and titronic universal piston burette (Schott Instrument GmbH, Mainz, Germany). For some SSP samples, the M_w values were measured with a gel permeation chromatography system (Waters) equipped with two TSKgel superAWMH columns (6.0 × 150 mm) and an RI detector (Waters 410), and hexafluoroisopropanol containing 0.01M CF₃CO₂Na was used as an eluent at a flow rate of 0.6 mL/min at 40 °C. The T_m and the heat of fusion (ΔH_f) were measured with a differential scanning calorimeter (Q2000, TA Instruments) equipped with a refrigerated cooling system (RCS90). Each sample was heated from 40 to 380 °C at a rate of 10 °C/min, cooled to 40 °C at a rate of 10 °C/min, and heated again to 380 °C. T_m and ΔH_f were obtained from a second heating scan. T_d was defined as the temperature at which the weight loss of sample by thermal decomposition exceeded 5% of the original weight and measured with a thermogravimetric analyzer (Q500, TA Instruments). The presence of a furan group in the prepared polymer was confirmed with ¹H-NMR (400 MHz, Bruker) by the dissolution of the sample in CF₃CO₂-*d*. Ultraviolet–visible diffuse reflectance/absorbance spectroscopy of the powdered polymer was performed with an ultraviolet–visible–near-infrared double-beam spectrophotometer (Varian, Cary 5000) equipped with a diffuse reflectance accessory. The structural characterizations of the samples were conducted with X-ray diffraction spectra (XRD-6000, Shimadzu, Japan) with Cu K α radiation ($\lambda = 0.1542$ nm).

RESULTS AND DISCUSSION

Prepolymerization

Three types of PA containing a furan moiety were synthesized with 4,6 salt and 4,F salt with a molar ratio of 4,6 salt to 4,F salt of 9:1 (PA-F-10), 8:2 (PA-F-20), and 7:3 (PA-F-30; Figure S1, Supporting Information). For comparison, salt-based PAs with only 4,6 and 4,F salts were also synthesized. The polymerization was conducted in two consecutive steps: prepolymerization at 170–220 °C for 7 h in the presence of water and SSP at 200–240 °C under a N₂ and water gas flow, as described in the Experimental section. The isolated PAP-4,6 was white, but the furan-incorporated prepolymers were slightly yellow.

Table I shows the IV, T_g , T_m , and ΔH_f values of the synthesized prepolymer. The IV of the prepolymer synthesized only from the 4,6 salt (PAP-4,6) was 0.21 dL/g. The incorporation of 10 mol % 4,F salt into the 4,6 salt (PAP-F-10) resulted in an increase in IV to 0.40 dL/g; however, further increases in the 4,F salt to 20 mol % (PAP-F-20) and 30 mol % (PAP-F-30) resulted in rapid decreases in the IV to 0.20 and 0.13 dL/g, respectively. This decreased polymerization degree with increasing FDCA content was ascribed to the poor polyamidation between FDCA and BDA; this was confirmed from a very low IV of 0.07 for the prepolymer synthesized from only the 4,F salt (PAP-F-100). Furthermore, as shown in the ¹H-NMR spectra in Figure S2 (Supporting Information), many unknown peaks were identified; this indicated the decomposition of the furanic moiety during high-temperature prepolymerization.³⁴

It is known that the IV of a polymer is a function of the molecular weight (M) and chain rigidity (a) of the polymer, as expressed by the Mark–Houwink–Sakurada relation:

$$IV = kM^a \quad (1)$$

where k is the proportional coefficient. Therefore, the differences in the IV of the polymers having different structures should be considered in terms of the chain rigidity and molecular weight. Because it was reported that the addition of aromatic diacid to the synthesis of PA of aliphatic diacid and diamine resulted in a decrease in the molecular weight because of the lower activity of the aromatic diacid compared to that of the aliphatic diacid,^{5,33} the higher IV of PAP-F-10 was ascribed to the increased chain rigidity by the aromatic furan group. In the cases of PAP-F-20 and PAP-F-30, the IVs were lower than that of PAP-F-10, although the chain rigidities of PAP-F-20 and PAP-F-30 were supposed to be higher than that of PAP-F-10

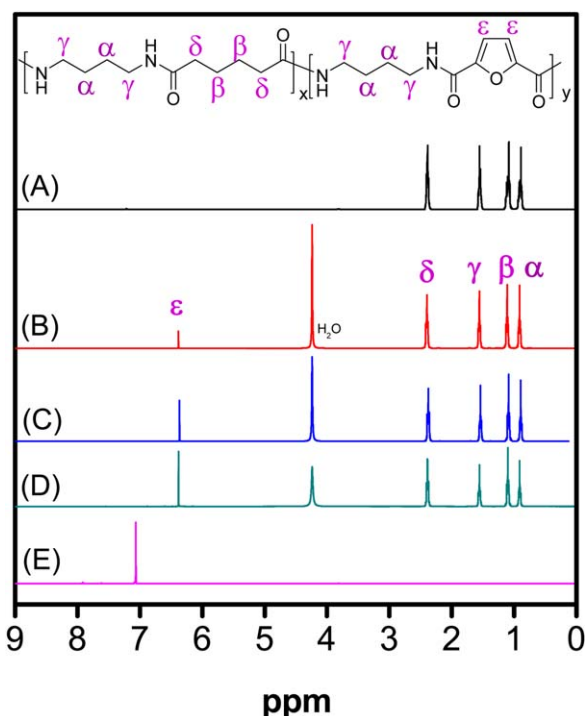


Figure 1. $^1\text{H-NMR}$ spectra of (A) PA-4,6, (B) PA-F-10, (C) PA-F-20, (D) PA-F-30, and (E) FDCA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

because of the higher content of furan groups. This implied that PAP-F-20 and PAP-F-30 had much lower molecular weights compared with PAP-4,6 and PAP-F-10, enough to compensate for the increase in IV caused by the increased chain rigidity.

T_g of the prepolymer was changed in a similar way, as observed in the IV by the addition of 4,F salt on PAP-4,6. PAP-F-10 showed a T_g of 65 °C; this was slightly higher than that of PAP-4,6 (56 °C). However, with increases in the furan content to 20 and 30 mol %, T_g decreased to 52 and 48 °C, respectively. On the other hand, with respect to T_m and ΔH_f , PAP-4,6 showed the highest values; this indicated the highest crystallinity of PAP-4,6 among the synthesized PAs.

The low IV of PAP-F-100 indicated that the reactivity of FDCA on polyamidation was feeble. Therefore, catalysts, such as butyl tin dihydroxide or triphenyl phosphite, have been used for making FDCA-based polymers.^{17,19} It is possible that the acid group in FDCA was activated in the form of acyl chloride.²⁰ In this study, solid-state polymerization was conducted to increase the molecular weight of the furan-incorporated PA.

SSP

SSP was conducted with the prepolymer. The resulting SSP polymers were marked as PA-4,6, PA-F-10, PA-F-20, and PA-F-30, depending on the prepolymer used. The SSP reaction was conducted at 220 °C for 12 h under a flow of water and nitrogen gas. Conventionally, the SSP of PA was at a temperature that exceeded 240 °C to remove water efficiently; thereby, the molecular weight of the resulting SSP polymer increased. However, on account of the relatively low T_m of the furan-incorporated prepolymer, in particular, for the PAP-F-30 sam-

ple, the SSP temperature was set to 220 °C. For the PAP-F-100 sample, because no T_m or T_g was detected from the differential scanning calorimetry experiment, SSP could not be done.

The successful incorporation of the furan moiety on PA-4,6 by SSP was confirmed from NMR and UV spectroscopy. The $^1\text{H-NMR}$ spectra of the PAs and FDCA are shown in Figures 1 and Figure S3 (Supporting Information). Four aliphatic methylene peaks were observed at 0.9, 1.1, 1.6, and 2.4 ppm, with nearly identical intensities in the $^1\text{H-NMR}$ spectra of PA-4,6. These were assigned as shown in Figure 1. In the NMR spectra of the furan-containing PA, the intensities of the methylene peaks corresponding to β and δ increased along with the appearance of a new peak at 6.4 ppm; this came from two hydrogens in the furan group. The intensities in this case were proportional to the amount of 4,F content in the PA (see Figure S3, Supporting Information). These intensity changes of α , β , γ , and δ strongly supported the contention that copolymerization occurred according to the intended 4,6 and 4,F ratio. The UV spectra of PA also supported the presence of a furan group in the PA-F series. As shown in Figure S4 (Supporting Information), which originated from the aromatic properties of the furan ring, this was observed in all of the samples in the PA-containing furan group.

The measured IV of the SSP polymer revealed that the SSP reaction increased the polymer chain length of the PA-4,6 and PA-F-10 samples. Figure 2 and Table S1 (Supporting Information) show that as the SSP time increased, the IV values of the PA-4,6 and PA-F-10 samples increased gradually and reached 0.40 and 0.54 after 24 h of reaction. In contrast, the polyamidation of PA-F-20 and PA-F-30 proceeded at a rate similar to that of PA-F-10 at an early reaction time of 2 h, but further polymerization occurred very slowly past that point.

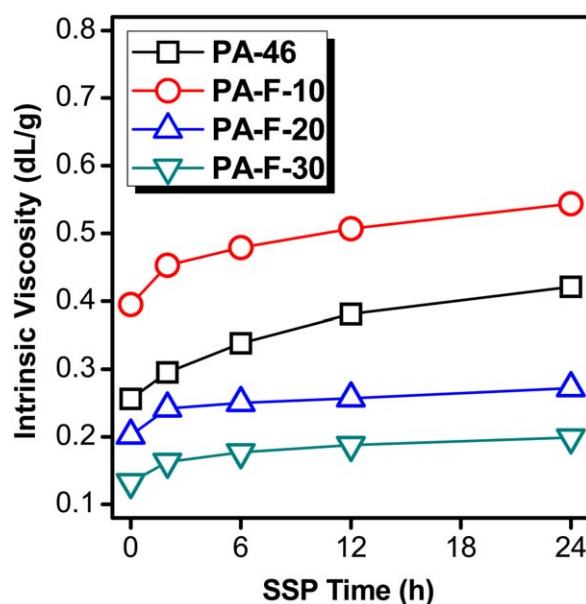


Figure 2. Effect of the FDCA content on the IV of PA-4,6/4,F. The SSP conditions were a temperature of 220 °C, a sweep gas flow rate of 2000 mL/min, and a particle size of 500 μm . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Properties of Copolyamides with Different FDCA Contents Synthesized by SSP with Prepolymers

SSP polymer	Prepolymer used	IV (dL/g)	T_g (°C)	T_m (°C)	ΔH_f (J/g)	T_d (5%)	M_w (Da)	Polydispersity index
PA-4,6	PAP-4,6	0.38	62	296	107	404	6,800	6.6
PA-F-10	PAP-F-10	0.51	73	293	73	365	13,560	5.3
PA-F-20	PAP-F-20	0.26	61	276	64	362	6,530	4.2
PA-F-30	PAP-F-30	0.19	54	262	57	358	4,470	3.9

The SSP conditions were a temperature of 220 °C, a time of 12 h, a sweep gas flow rate of 2000 mL/min, and a particle size of 500 μ m.

The molecular weight of the SSP polymer was measured with gel permeation chromatography. Table II and Figure S5 and Table S1 (Supporting Information) show that the order of M_w values of copolyamide was similar to that of the IV values. The highest IV copolyamide, PA-F-10, showed an M_w of 13 K g/mol with a polydispersity of 5.3. In the case of PA-4,6 and PA-F-20, although PA-4,6 showed a higher IV value, their M_w values were very similar, about 6.5 kg/mol. The lowest IV copolyamide PA-F-30 was found to have an M_w value of 4.4 kg/mol.

As mentioned previously, the lower IV value of PA-4,6 compared to that of PA-F-10 at the same reaction temperature of 220 °C was ascribed to the lower chain rigidity of PA-4,6 compared to that of PA-F-10. We confirmed this from the T_g values. Table II shows the T_g increase from 56 to 64 °C with the 10 mol % incorporation of PA-4,F in PA-4,6; this indicated that the internal molecular movement could have deteriorated at the PA-F-10 sample. The low IV and T_g of PA-F-20 and PA-F-30 were also supposed to result from the low molecular weight, despite the higher chain rigidity, in a manner similar to the prepolymers of PAP-F-20 and PAP-F-30.

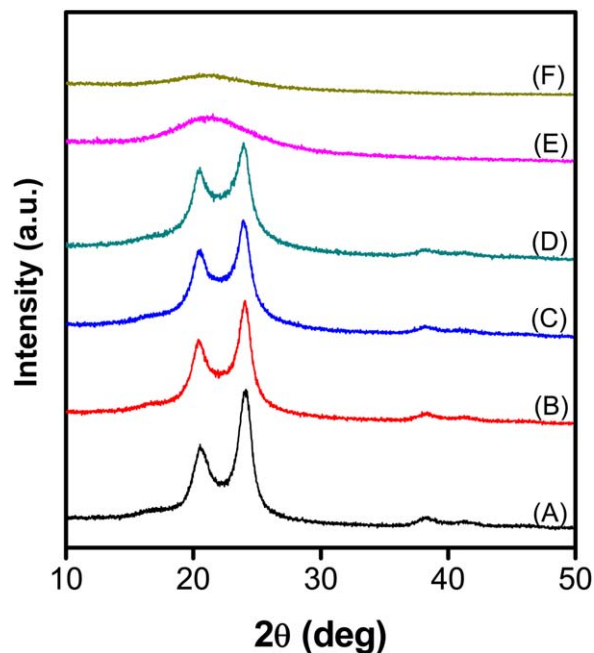


Figure 3. X-ray diffraction of (A) PA-4,6, (B) PA-F-10, (C) PA-F-20, (D) PA-F-30, (E) PAP-F-100, and (F) a sample holder. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

On the other hand, we observed that the ΔH_f values decreased with increasing furan content from 107 J/g for PA-4,6 to 57 J/g for PA-F-30; this indicated that the crystallinity of PA decreased with the incorporation of the furan group. This phenomenon also observed from the X-ray diffraction patterns shown in Figure 3. It is known that PA-4,6 is a crystalline polymer with diffraction peaks located at 2θ values of 20.3 and 24.0°. In contrast, no peak was observed in the X-ray diffraction pattern of PA-F-100; this indicated the amorphous structure of the furan-based PA. Therefore, it was feasible that the peak intensity of PA-4,6 decreased with the increase in the furan content in the PA-F series, as shown in Figure 3.

We reported that the presence of an aromatic group, such as a phenyl group, on PA decreased the IV value but increased the thermal stability and T_m of the PA. For example, Gaymans *et al.*⁵ showed that an addition of 30% of a terephthalate-based salt to a 4,6 salt decreased the IV value from 1.3 to 0.72 after SSP, whereas the T_m of the polymer increased from 290 to 302 °C. Our previous research also revealed that an increase in the PA-4,T content in PA-4,6 from 28 to 47% gave rise to an increase in T_d from 402 to 423 °C and an increase in T_m from 302 to 314 °C. However, in this research, the introduction of the furan moiety on the PA-4,6 resulted in a decrease in the thermal stability and T_m . Table II, Figures (4 and 5), and S6 (Supporting Information) show several thermal properties of the synthesized SSP polymers. With the addition of 10 mol % 4,F salt, T_m of PA-4,6 decreased from 296 to 293 °C. A further increase in the 4,F salt to 30 mol % gave the PA a T_m value of 262 °C. Similarly, the T_d of PA-4,6 was reduced from 404 to 365 °C when 10 mol % 4,F component was incorporated. The poor thermal stability of the furan-incorporated PA compared to the terephthalate group was assumed to have originated from the low thermal stability of the furan group with respect to the phenyl group or aliphatic $-\text{CH}_2-$ chain. Furthermore, the presence of an acid group in FDCA, which is known to be decarboxylated at 200 °C, facilitated the decomposition of the PA during polyamidation.³⁶ In fact, as shown in Figure 4, PAP-F-100 started to degrade at 200 °C.

Effect of the Reaction Parameters on the SSP of PA-4,6/4,F

The effect of the SSP temperature on the IV was investigated with PA-F-10. This result is shown in Figure 6. With an increase in the SSP temperature from 200 to 220 and 240 °C, IV increased from 0.47 to 0.54 and 0.62 after 24 h of the SSP reaction. Interestingly, at temperatures of 200 and 220 °C, the SSP rate appeared to slow down after 24 h, but at 240 °C, IV

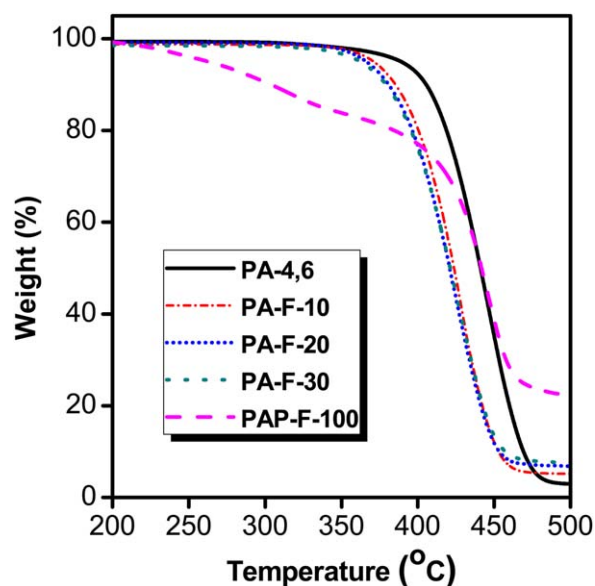


Figure 4. Thermogravimetric analysis curves of PA-4,6 and PA-F. The SSP conditions were a temperature of 220 °C, a time of 12 h, a sweep gas flow rate of 2000 mL/min, and a particle size of 500 μm . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increased linearly after 12 h and reached 0.75 dL/g after 48 h of the SSP reaction. This result indicated that the temperature of SSP affected the IV of PA more significantly than the reaction time did. However, a further increase in the reaction temperature to 240 °C could not be carried out with the furan-containing PA because of the melting phenomenon of the polymer during the SSP. In contrast, the SSP of PA-4,6 was con-

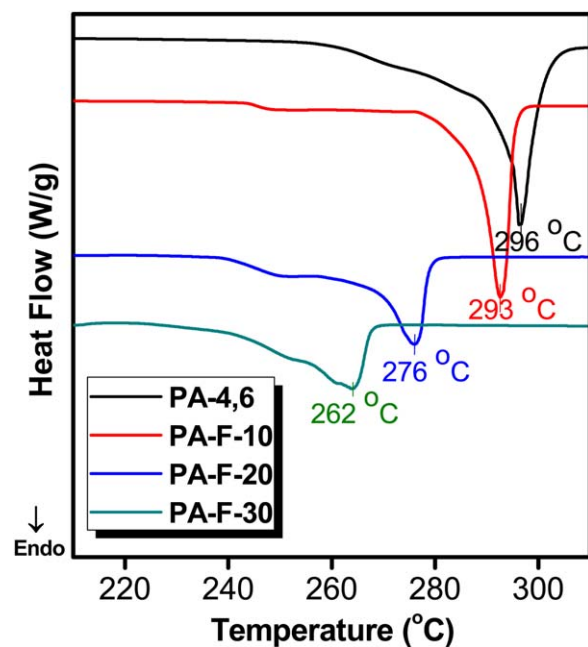


Figure 5. T_m values of PA-4,6 and PA-F. The SSP conditions were a temperature of 220 °C, a time of 12 h, a sweep gas flow rate of 2000 mL/min, and a particle size of 500 μm . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

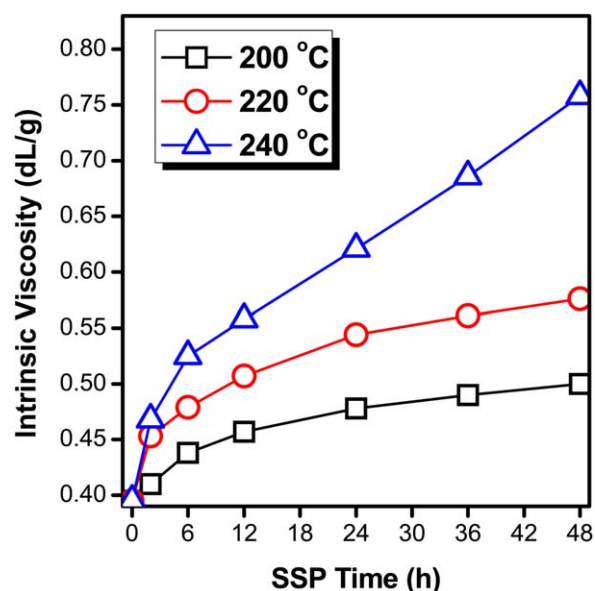


Figure 6. Effect of the SSP temperature on the IV of PA-F-10. The SSP conditions were a sweep gas flow rate of 2000 mL/min and a particle size of 500 μm . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ducted at a temperature over 240 °C, and the IV values reached 0.53 and 0.81 when SSP was conducted at 260 °C for 6 and 24 h, respectively. On the other hand, the effects of the SSP time on the other thermal properties were found to negligible. Table S2 (Supporting Information) showed that the T_g , T_m and ΔH_f were marginally increased with increasing SSP time.

The effective removal of the water byproduct from the solid particle was an important factor in the attempt to increase the

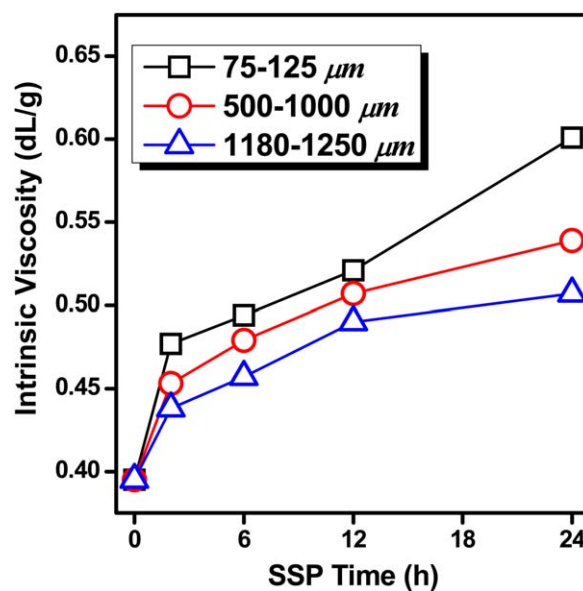


Figure 7. Effect of the particle size on the IV of PA-F-10. The SSP conditions were a temperature of 220 °C, a sweep gas flow rate of 2000 mL/min, and particle sizes of 75–125, 500–1000, and 1180–1250 μm . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

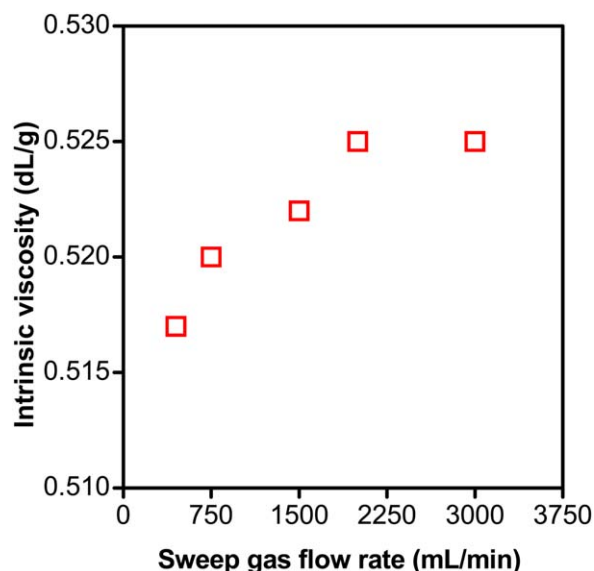


Figure 8. Effect of the sweep gas flow rate on the IV of PA-F-10. The SSP conditions were a temperature of 240 °C, a time of 6 h, and a particle size of 500 μm . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymer chain length. When the particle size of the polymers was small and the sweep gas flow rate was high, the removal of water produced as a byproduct was facilitated; this enhanced the polyamidation. However, during the synthesis of the PA-4,6/PA-4,F copolyamide, the effects of the particle size and the purge gas flow rate were not significant, as shown Figures 7 and 8. When the particle size was reduced from 1180–1250 to 75–125 μm , the IV increased from 0.50 to only 0.60 after 24 h of the SSP reaction at 220 °C; this indicated that the effect of internal diffusion was not dominant during the SSP of PA-F-10. Similarly, as shown in Figure 8, when the flow rate of the sweep gas increased from 450 to 2000 mL/min, the IV marginally increased from 0.52 to 0.53 dL/g. Furthermore, the IV values at 2000 and 3000 mL/min were nearly identical. The flow rate of the sweep gas is known to affect the external diffusion of the byproduct, which is related to the removal of the water byproduct from the surface of the polymer particle. However, during this reaction, the effect of the external diffusion of water during SSP appeared to be insignificant with respect to the increase in the chain length of PA-4,6/4,F.

CONCLUSIONS

In summary, we demonstrated that the incorporation of FDCA-based PA (PA-4,F) into the aliphatic PA, PA-4,6 was successfully conducted through SSP. A 10 mol % addition of PA-4,F to PA-4,6 increased the IV; this was presumably because of the increase in the chain rigidity. This was also confirmed from the increase in T_g . However, further increases in the furan content to 20 and 30 mol % resulted in a sharp decrease in the polymerization rate because of the lower reactivity of FDCA compared to that of the AA. The SSP rate of PA-4,6/4,F was assumed to be dominated by the intrinsic reaction, whereas the effects of the internal and external diffusion were insignificant. On the other hand, the ther-

mal stability of PA-4,6/4,F was degraded because of the poor thermal properties of the furan component.

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