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Solid-State Polymerization of Semiaromatic Copolyamides of Nylon-4,T and Nylon-4,6: Composition Ratio Effect and Thermal Properties

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Ⓢ *Supporting Information*

ABSTRACT: Solid-state polymerization (SSP) of semiaromatic copolyamides composed of nylon-4,T and nylon-4,6 in different molar ratios were investigated using a mixture of nitrogen and steam as the sweep fluid at reaction temperatures in the range of 220−260 °C. Prepolymers having different nylon-4,T contents (28.2, 37.9, and 47.8 mol %) were synthesized by melt polyamidation with stoichiometric ratios of diamine and diacid. The SSP conditions were carefully chosen to eliminate the influences of both internal and external diffusion of the reaction byproducts. Under these conditions, a high-molecular-weight semiaromatic copolyamide with an intrinsic viscosity of 2.469 dL/g was obtained upon SSP at 260 °C for 48 h. As the nylon-4,T content increased, the SSP rate decreased owing to the inherently low reactivity of the aromatic diacid and inhibition of chain-end mobility. The glass transition, melting, and decomposition temperatures of the polymers synthesized from the higher-nylon-4,T-content prepolymer were always higher than those of the polymers synthesized from the lower-nylon-4,T-content prepolymer.

1. INTRODUCTION

High-temperature polyamides (or nylons) are important engineering polymers with unique properties including high melting temperature, high heat and chemical resistance, excellent dimensional stability, low water absorption, and high mechanical strength and stiffness. Thus, they are widely used in electronics (e.g., connectors, sockets, switches, surface mount devices, reflectors, and portable electronics housing) and lightweight automobile applications (e.g., powertrain components and electrical systems). Many properties of polymeric materials can be improved by increasing the molecular weights of the polymers, which can widen their applications. However, it is difficult to reach polymers with desired molecular weights for such applications using typical melt polymerization because of their high melting temperatures and the chain degradation that occurs at high reaction temperatures. One of the routes to achieve polyamides with high molecular weights is solid-state polymerization (SSP).[1,2] In a typical SSP process, a polymer with low molecular weight (a prepolymer) is first synthesized by melt polymerization at relatively low temperature. If necessary, the prepolymer is then ground or pelletized and then crystallized. Next, the prepolymer is heated at a temperature above its glass transition temperature, but below its melting temperature with a sweep-gas fluid (e.g., inert gases) or with application of vacuum to remove reaction byproducts. Various polyamides have been synthesized by SSP, including nylon-4,2,[3] nylon-6,6,[4] nylon-4,6,[5,6] nylon-4,T,[7] nylon-4,I,[8] copolyamides,[9,10] and terpolyamides.[11,12] In addition to polyamides, SSP has been widely used to produce various important engineering plastics including polyesteramide,[13] poly(ethylene terephthalate) (PET),[14−16] poly(trimethylene

terephthalate) (PTT),[17,18] poly(butylene terephthalate) (PBT),[19] poly(bisphenol A carbonate) (BPA-PC),[20−24] poly(ethylene naphthalate) (PEN),[25] and poly(L-lactic acid) (PLA).[26−33] Theoretical modeling studies have also been undertaken to provide deeper insight into the behavior of industrially relevant polymers such as BPA-PC,[34−36] nylon,[37,38] and PET[39−41] during SSP.

Various SSP approaches have been tested to achieve high-molecular-weight, high-temperature polyamides, and some high-temperature polyamides such as aliphatic diamine−aliphatic diacid polyamides (nylon-6,6, T_m = 262 °C; nylon-4,6, T_m = 289 °C) have been commercialized. However, the development of semiaromatic polyamides produced from aliphatic diamine−aromatic diacid (e.g., terephthalic acid and isophthalic acid) with enhanced thermal, chemical, and mechanical properties is still needed to meet market requirements.[7,8,19] Semiaromatic polyamides composed of aliphatic diamine−aromatic diacid polymers, which include aliphatic diamines having six carbons or less, might not be commercially attractive materials owing to their extremely high melting temperatures (e.g., nylon-4,T, T_m = 428/475 °C; nylon-6,T, T_m = 370 °C), which makes it difficult for them to be melt-processed (e.g., using an extruder), and their relatively high water absorption properties. For these reasons, polyamides composed of aromatic/aliphatic dicarboxylic acids and aliphatic diamines have been widely investigated in both the academic
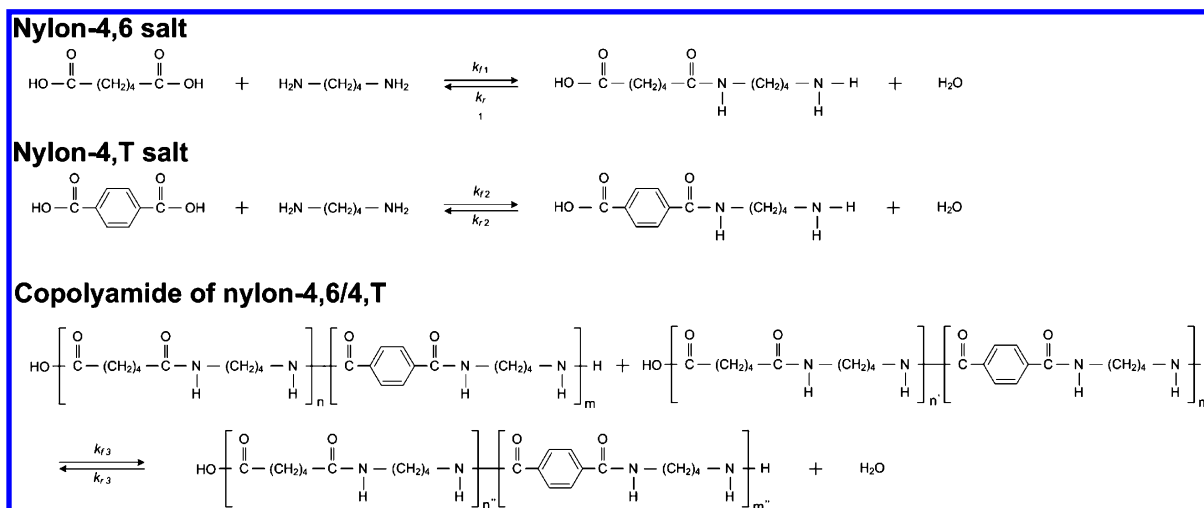
Scheme 1. Synthetic Scheme for the Copolyamide of Nylon-4,6/-4,T

and industrial sectors. Examples include nylon-6,6/-6,n (where n is the number of carbons ranging from 2−10),[42] nylon-4,T/-4,6,[9] nylon-4,T/-6,T,[10] nylon-10,T/-6,T and nylon-12,T/-6,T,[43] nylon-4,6/-4,T/-4,I,[11] and nylon-4,6/-4,T/-6,T and nylon-4,6/-4,T/-6,6.[12]

The overall rate of SSP depends on the following four chemical or physical steps: (1) functional end-group diffusion in the amorphous region of the polymer matrix, (2) intrinsic reaction kinetics of the chain extension reaction through collision of functional end groups, (3) internal diffusion of the reaction byproducts through the polymer matrix to the polymer surface, and (4) external diffusion of the reaction byproducts from the polymer surface into the sweep-gas phase. In step 2, end-group migration through interchange reactions of amine−amide or alcohol−ester in the amorphous region can facilitate the chain extension reaction.[44,45] As we and other groups previously reported for the SSPs of nylon-6,6,[4] PET,[14−16] PTT,[17,18] and BPA-PC,[20−24] the SSP rate is dependent on one or more SSP process parameters (temperature, pressure, and sweep-gas flow rate) and prepolymer properties (particle size, crystallinity, molecular weight of the prepolymer, catalysts, and composition). Thus, it is very important to decouple the factors influencing the SSP rate to gain better insight into the molecular weight evolution during SSP and to predict attainable molecular weights. However, only a few fundamental studies of SSP processes for semiaromatic polyamides have been conducted. Gaymans et al.[9] reported thermal and mechanical properties of copolyamides of nylon-4,T/-4,6 at different molar ratios synthesized under one set of SSP conditions (4 h, 260 °C, stream of N_2 and steam with ratio of 2:1, with no information provided on the sweep-gas flow rate and prepolymer properties).

In this research, we investigated the effect of prepolymer properties (particle size and aromatic diacid composition) and SSP parameters (temperature, time, sweep-gas flow rate, and steam content of the sweep fluid) on SSP nylon-4,T/-4,6. Scheme 1 shows nylon-4,T/-4,6 synthetic chemistry. To examine the effect of aromatic diacid composition, the SSP conditions were carefully controlled to eliminate any influence of either internal or external byproduct diffusion. The polymer properties, including glass transition temperature (T_g), melting temperature (T_m), and heat of fusion (ΔH_f), were measured during the first and second scans of differential scanning

calorimetry (DSC) studies. The thermal stability of the synthesized polymers at different aromatic diacid compositions was measured using thermal gravimetric analysis (TGA). The polymer composition was determined using ^{1}H NMR spectroscopy.

2. EXPERIMENTAL SECTION

2.1. Materials. 1,4-Butanediamine (BDA, purity > 98%) was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Terephthalic acid (TPA, purity > 99%) and adipic acid (AA, purity > 99%) were purchased from Junsei Chemical Co., Ltd. (Tokyo, Japan). 1,6-Hexamethylene diamine (HMDA purity > 99%), ethanol (purity > 99.9%), methanol (purity > 99.9%), and concentrated sulfuric acid (purity > 98%) were purchased from Daejung Chemicals & Metals Co., Ltd. (Siheung, Korea). Trifluoroacetic acid-d (CF_3COOD, purity > 99%), as an NMR solvent, was purchased from Sigma-Aldrich (St. Louis, MO). Deionized ultrafiltered (DIUF) water was prepared using a Millipore Milli-Q Ultrapure water purification system with a 0.22-μm filter (Billerica, MA). Nitrogen (purity > 99.99%) was purchased from Shinyang Sanso Co. (Seoul, Korea) and passed through an oxygen trap (model 20601, Restek Corp., Bellefonte, PA) before introduction into the reactor.

2.2. Preparation of Nylon Salts. Steps in nylon-4,6 salt preparation were as follows: BDA (88.1 g, 1 mol) was dissolved in 705.3 g of methanol with vigorous stirring at 25 °C. Next, 146.1 g of AA (1 mol) was slowly added to the solution of BDA in methanol for 2 h to synthesize the nylon-4,6 salt. The solution was cooled to 25 °C to precipitate the synthesized nylon-4,6 salt, which was filtered off using 7−9-μm-pore-size filter paper, washed with cold methanol, and dried at 50 °C in a vacuum oven for 48 h. The mass yield of nylon-4,6 salt was 96.2%.

Nylon-4,T salt preparation was performed as follows: BDA (88.1 g, 1 mol) was dissolved in 1 L of DIUF water with vigorous stirring at 25 °C. Next, 166.1 g of TPA (1 mol) was slowly added to the aqueous BDA solution for 2 h to synthesize the nylon-4,T salt. After the solution had been cooled to 25 °C, the nylon-4,T was precipitated by addition of 2 L of cold ethanol to the solution. The precipitated nylon-4,T salt was filtered off, washed with cold ethanol, and dried at 50 °C in a vacuum oven for 48 h. The mass yield of Nylon-4,T salt was

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Table 1. Properties of the Prepolymers

prepolymer	nylon-4,T/-4,6 ratio[a] (mol/mol)	IV (dL/g)	$T_{m,first}$ (°C)	$T_{m,second}$ (°C)	$\Delta H_{f,first}$ (J/g)	$\Delta H_{f,second}$ (J/g)	$T_{d,5}$ (°C)	$T_{d,10}$ (°C)
PAP1	28.2:71.8	0.085	273	307	93.6	64.6	236	340
PAP2	37.9:62.1	0.068	253	305	161.7	14.0	232	277
PAP3	47.8:52.2	0.070	246	306	147.9	4.8	237	287

[a]Determined by NMR spectroscopy.
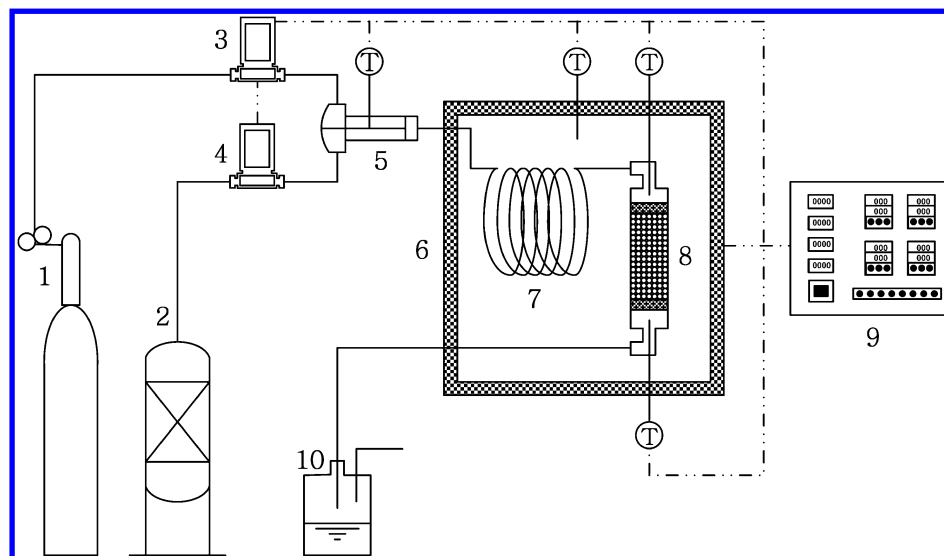
Figure 1. Schematic diagram of the SSP apparatus: (1) nitrogen source, (2) water source, (3) gas mass flow controller, (4) liquid mass flow controller, (5) mixer, (6) forced-convection oven, (7) preheater coil, (8) reactor, (9) controller, and (10) water trap.

96.4%. During the nylon-4,6 and nylon-4,T salt preparations, unreacted BDA, AA, and TPA can cause stoichiometric imbalance of the acid and amine end groups.

2.3. Prepolymer Synthesis. Prepolymers composed of nylon-4,T and nylon-4,6 at different composition ratios were synthesized by polyamidation of the nylon salts using DIUF water as the solvent. The prepolymerization was carried out in a custom-built, 1200 cm³ high-pressure stirred reactor. The reactor was equipped with a heat furnace, magnetic stirrer, purge line, and vent line. In a typical prepolymerization, a mixture of nylon-4,T salt and nylon-4,6 salt at different molar ratios (samples PAP1, PAP2, and PAP3) and 30 g of DIUF water were added to the reactor. The total amount of nylon salts used in prepolymerization was maintained at 300 g. The reactor was then purged with nitrogen for 30 min at a flow rate of 300 mL/min and pressurized at 0.5 MPa of nitrogen. The temperature of the reactor was increased from 25 to 210 °C with stirring at 900 rpm for 1.5 h. Over the course of temperature ramping, the reactor pressure increased to 2 MPa. The polyamidation was allowed to proceed at 210 °C for 6 h at 2 MPa. After prepolymerization, the reactor was rapidly depressurized to atmospheric pressure to remove water. The properties of the prepolymers are listed in Table 1. Hereafter, the solid-state-synthesized samples obtained using PAP1, PAP2, and PAP3 as the prepolymers are designated as PA1, PA2, and PA3, respectively.

2.4. Solid-State Polymerization. Prior to SSP, the prepolymers were ground into powders and separated into three different particle sizes (<75, 250−500, and 1000−1180 μm) using a sieve. A schematic diagram of the SSP apparatus is shown in Figure 1. The apparatus consists of a nitrogen source, water source, gas mass flow controller, liquid mass flow controller, mixer, forced-convection oven, preheater coil,

reactor, controller, and water trap. The reactor (8) was a stainless steel 316 tube with an internal diameter of 1.6 cm and a length of 10 cm, giving an inner volume of 20 mL. Metal mesh was placed at the top and bottom of the reactor to hold the prepolymer particles in the middle of the reactor. The SSP temperature was controlled by housing the reactor (8) and the preheater coil (7) in the forced-convection oven (6). The nitrogen flow rate was controlled using a gas mass flow controller (3, model TSC-220, MK Precision Co. Ltd., Seoul, Korea), and the water flow rate was controlled using a liquid mass flow controller (4, LIQUI-FLOW L2C2, Bronkhorst High-Tech B.V., Ruurlo, The Netherlands). The nitrogen flow and the water flow were mixed in a T-type mixer prior to flowing into the SSP reactor. The temperature of the mixer was maintained at 220 °C.

For each SSP experiment, the reactor was charged with 1.5 g of the ground prepolymer and placed in the forced-convection oven. The whole system was purged with nitrogen at a flow rate of 2000 mL/min for 10 min, and then the reactor temperature was increased to 110 °C for 5 min. When SSP was conducted in N₂ flow only, the flow rate was changed to 3000 mL. To examine the effect of steam content on SSP, the purge gas was changed from N₂ to a mixture of N₂ and steam at a 2:1 or 10:1 volume ratio and a flow rate of 3000 mL/min. After the gas mixture had flowed into the reactor for 1 min, the reactor temperature was increased to the desired SSP temperature. Typically, it took approximately 10 min to reach the desired reaction temperature. During the temperature ramping, marginal changes in the intrinsic viscosity (IV) of the polymer were confirmed. For example, the IVs of PAP1, PAP2, and PAP3 changed from 0.085 to 0.084 dL/g, from 0.068 to 0.069 dL/g, and from 0.070 to 0.072 dL/g, respectively, when the SSP temperature was 260 °C. As the reactor temperature

Scheme 2. Formation Scheme for the Pyrrolidine End Group and Its Reaction with Water to Form the Carboxylic End Group
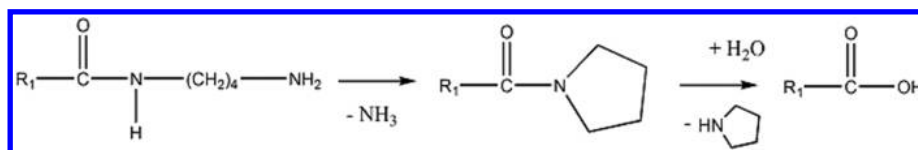
approached 0.5 °C below the desired SSP temperature, SSP was initiated by flowing the nitrogen and steam mixture through the reactor at various flow rates in the range of 450−3000 mL/min. SSP was completed for the desired reaction times, the sweep-gas flow was stopped, and the reactor was isolated in an environment of nitrogen and steam. The reactor was then rapidly cooled to 110 °C and purged with nitrogen at a flow rate of 2000 mL/min for 1 min. After the temperature had decreased to ambient conditions, the solid-state-polymerized sample was obtained and subsequently analyzed.

2.5. Characterization. The IVs of the polymers were measured using an Ubbelohde viscometer equipped with an automatic data acquisition system (model ViscoSystem AVS 370) and TITRONIC universal piston buret (SCHOTT Instruments GmbH, Mainz, Germany). IVs were determined from the intercept of the extrapolated straight-line plot of the reduced specific viscosities at concentrations of 4, 6.4, 8, and 10 mg/mL. Each IV measurement was performed in triplicate, and average values are reported. The typical error range in the IV measurements was 0.003−0.01 dL/g. The polymer sample was dissolved in concentrated sulfuric acid at 25 °C. The thermal properties of the polymers were measured using a Q2000 differential scanning calorimeter equipped with a refrigerated cooling system (RCS90) manufactured by TA Instruments (New Castle, DE). A nitrogen flow of 50 mL/min was used for DSC calibration and sample measurements to prevent oxidative degradation of the samples. The temperature during the heating scan and ΔH_f measurements was calibrated using a tin standard. In a typical measurement, samples of ∼5 mg were sealed in aluminum hermetic pans. The melting temperature and heat of fusion for the first scan ($T_{m,first}$ and $\Delta H_{f,first}$, respectively) of the samples were determined from the first heating scan using a 10 °C/min heating rate from 40 to 380 °C. After the temperature had decreased to 40 °C at a cooling rate of 10 °C/min, the melting temperature and heat of fusion for the second scan ($T_{m,second}$ and $\Delta H_{f,second}$, respectively) and the glass transition temperature of the samples were determined from the second scan using a 10 °C/min heating rate from 40 to 375 °C. TGA was carried out on a DuPont Instruments TGA 2950 thermal analyzer. In a typical measurement, samples of ∼10 mg in platinum crucibles were heated at a rate of 10 °C/min from 30 to 700 °C in a nitrogen flow of 50 mL/min. The decomposition temperatures at 5% weight loss ($T_{d,5}$) and 10% weight loss ($T_{d,10}$) of the copolyamides were determined using the TGA curves. The quantification of the diacid (TPA and AA) and diamine (BDA) contents in the synthesized prepolymer and copolyamides and the estimation of pyrrolidine formation were carried out using a Bruker Avance 500 MHz NMR spectrometer equipped with an Oxford narrow-bore magnet, a Red Hat Linux host workstation, and XWIN-NMR software (version 3.6).

3. RESULTS AND DISCUSSION

3.1. Effects of Steam Content of the Sweep Fluid. In typical SSPs of polyesters,[14,17−19,25,46−48] polycarbonates,[20−24]

and polylactic acids,[26−28] inert gases such as N_2, Ar, CO_2, and He are used as the sweep gas or a vacuum is used to remove reaction byproducts. To prevent plausible unwanted side reactions during SSP (e.g., hydrolysis, oxidation, discoloration), the oxygen and water contents of the sweep fluids should be minimized. In the case of high-temperature nylon SSP, however, some amount of water in the sweep-fluid phase might be necessary to restrain side reactions and thermal degradation (e.g., amine end-group cyclization to form pyrrolidines).[6,9−12]

The removal of water, which is produced as a reaction byproduct, drives the polymerization reaction in the forward direction (Scheme 1); thus, the presence of water in the sweep-gas fluid can diminish the SSP rate. To understand the effect of water in the sweep-gas fluid on SSP rate, the IV evolution during SSP of PAP1 at different steam contents of the sweep fluid was examined, and the results are shown in Figure 2. It can
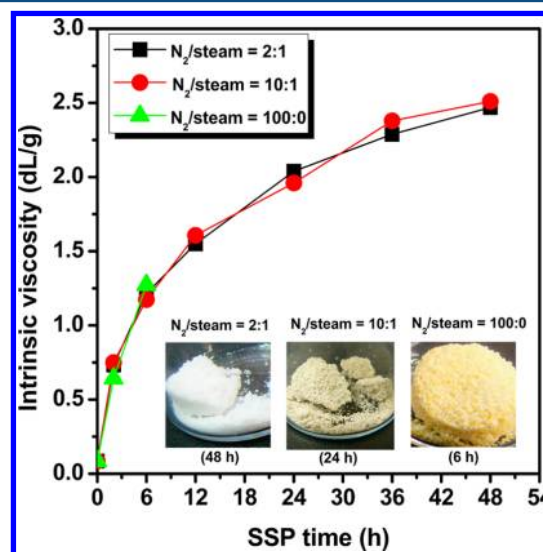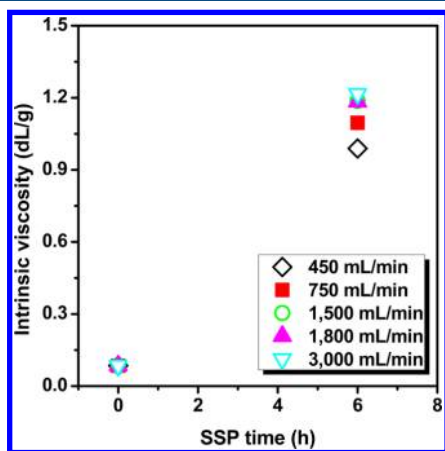

Figure 2. Effect of the steam content of the sweep fluid on the intrinsic viscosity evolution during SSP at 260 °C. SSP conditions: prepolymer = PAP1; particle size = 250−500 μm; sweep-gas flow rate = 3000 mL/min; and N_2/steam ratio = 2:1, 10:1, and 100:0 (v/v).

be see that even ratios of N_2 to steam as high as 1:1 (v/v) did not have a significant effect on the evolution of the molecular weight. This might be a result of the high equilibrium constant of the nylon synthesis reaction. For example, equilibrium constant values of the nylon synthesis reaction are in the range 100−750 under nitrogen/steam flow,[49,50] which is much higher than those of polycarbonate (0.87−2.35) and polyester (0.5−1.25) under nitrogen flow.[19,34,41,47,51,52] Samples synthesized with low or no steam content in the sweep fluid had different visual and solubility properties. As shown in Figure 2, all of the samples synthesized with 2:1 N_2/steam retained their white color, whereas the color of the samples polymerized by SSP for 24 h with 10:1 N_2/steam changed to bright gray. The samples synthesized with N_2/steam ratios of 2:1 and 10:1 were highly

soluble in concentrated sulfuric acid. In contrast, when only N_2 was used as the sweep fluid, the color of the samples gradually changed to dark yellow after the first 6 h of SSP. After 6 h, all of the samples appeared black and were not soluble in concentrated sulfuric acid. This indicates that side reactions (e.g., pyrrolidine formation and cyclization) occurred in the absence of steam during the SSP of the nylon-4,T/-4,6 copolyamide. In subsequent experiments, SSP was performed with a 2:1 N_2/steam sweep fluid.

3.2. External Diffusion: Nitrogen and Steam Mixture Flow Rate Effects. The mass transfer of byproducts (water in the case of nylon synthesis) from the particle to the sweep-gas fluid phase and the intrinsic reaction kinetics between two end groups determine the SSP reaction rate at a fixed temperature. The mass transfer includes external diffusion of the byproduct from the polymer particle surface to the fluid phase and internal diffusion of the byproduct from the polymer particle matrix to the particle surface. The influence of internal diffusion can be eliminated by using polymer particles of sufficiently small sizes, and that of external diffusion can be eliminated by using a sufficiently high sweep-gas flow rate.

The effect of the sweep-fluid flow rate on the SSP of the nylon-4,T/-4,6 copolyamide was investigated at 260 °C using PAP1 with particle sizes of 250−500 μm as the prepolymer, as shown in Figure 3. At all flow rates in the range of 450−3000

Figure 3. Effect of the flow rate of the nitrogen/steam mixture on the intrinsic viscosity evolution during SSP at 260 °C. SSP conditions: prepolymer = PAP1, particle size = 250−500 μm, sweep-gas flow rate = 450−3000 mL/min, and N_2/steam ratio = 2:1 (v/v).

mL/min, the IVs increased rapidly during 6 h of SSP. The IVs of the polymers synthesized at the lower flow rates of 450−750 mL/min were lower than those of the polymers synthesized at the higher nitrogen/steam flow rate of 1500 mL/min. A further increase of the sweep-gas flow rate to over 1800 mL/min did not appear to increase the IVs. The SSP of the PAP2 and PAP3 prepolymers with higher nylon-4,T contents resulted in a similar sweep-gas fluid dependence. At above 1500 mL/min, the IVs of the synthesized polymers were very similar. This indicates that sweep-fluid flow rates higher than 1500 mL/min are sufficient to eliminate the effects of byproduct external mass transfer at 260 °C. This flow rate should also be sufficient to eliminate external mass-transfer effects at lower reaction temperatures of 220 and 240 °C, where the SSP rate and byproduct generation rate are lower. The nitrogen/steam flow rate was kept at 3000 mL/min in subsequent SSP experiments.

3.3. Internal Diffusion: Particle Size Effects. The influence of the internal diffusion of the byproducts on the SSP of the copolyamide was evaluated using the PAP1 prepolymer with three different sizes, as shown in Figure 4.
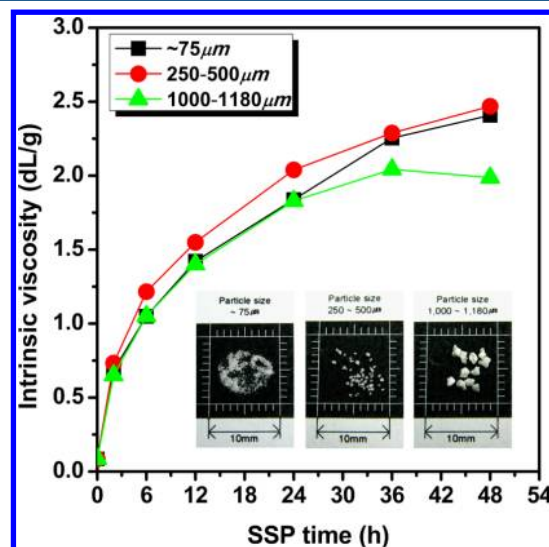
Figure 4. Effect of particle size on the intrinsic viscosity evolution during SSP at 260 °C. SSP conditions: prepolymer = PAP1; particle size >75, 250−500, and 1000−1180 μm; sweep-gas flow rate = 3000 mL/min; and N_2/steam ratio = 2:1 (v/v).

When the particle size decreased from 1000−1180 to <75 μm, only a marginal increase in IVs was observed after the first 24 h of SSP. When the SSP time was increased to 48 h, the IVs of the copolyamide synthesized using 1000−1180-μm prepolymer were only ∼19% smaller than those of the copolyamide synthesized using the prepolymer with a particle size of <75 μm. The prepolymers with higher nylon-4,T contents (PAP2 and PAP3) showed similar IV values when the particle size was below 500 μm. This effect of particle size is far less significant than that observed in the SSPs of PET and BPA-PC. For example, in the case of PET, a decrease in particle size from 1000 to 100 μm led to a ∼100% increase in IV (from 0.47 to 0.97) when PET was synthesized by SSP.[46] In the case of BPA-PC, a decrease in particle size from 3.6 mm to 20 μm led to a ∼150% increase in average molecular weight (from 7200 to 18000 g/mol).[20] The much weaker dependence on particle size of the SSP rate of the copolyamide can be attributed to the much larger equilibrium constant for the polyamidation, which can tolerate high byproduct concentrations in the polymer matrix. In subsequent experiments, SSP was performed using prepolymers with a particle size in the range of 250−500 μm.

3.4. Temperature Effects and Thermal Properties. Figure 5 shows the effect of reaction temperature on the IV evolution of PAP1 during 48 h of SSP. Typically, an increase in the SSP temperature leads to an enhancement of the SSP rate by increasing the end-group mobility, the end-group reactivity, and/or the diffusion rate of the byproduct.[1,2] In the case of semiaromatic copolyamide SSP, polyamidation to produce high-molecular-weight polymers is rather challenging because NH_2 end groups tend to transform into inactive pyrrolidine end groups during prepolymerization and SSP at high reaction temperatures.[8,9] To compensate for the formation of inactive end groups and to increase the molecular weight, a slight excess of diamine (diacid-to-diamine molar ratio of 1.00:1.02−1.08) is
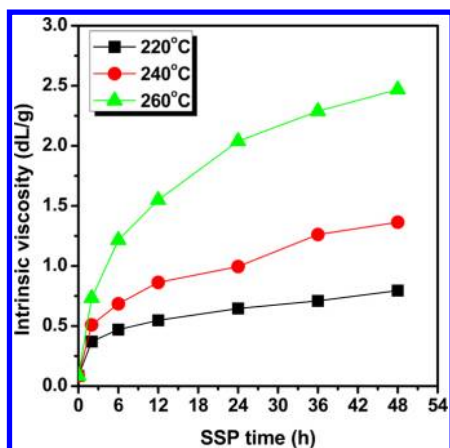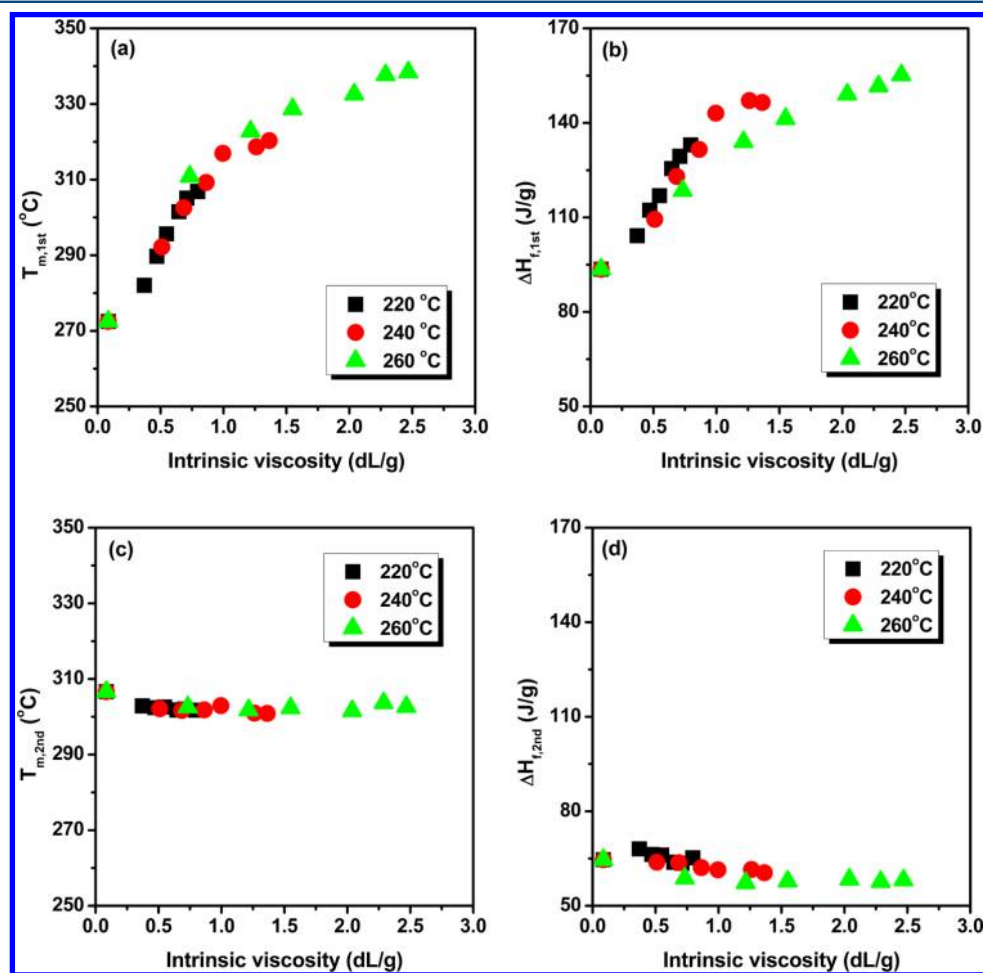
Figure 5. Effect of temperature on intrinsic viscosity evolution during SSP at 220−260 °C. SSP conditions: prepolymer = PAP1, particle size = 250−500 μm, sweep-gas flow rate = 3000 mL/min, and N_2/steam ratio = 2:1 (v/v).

typically used in the prepolymerization.[5,9,11,12] Herein, despite the use of a stoichiometric diamine content in the salt preparation, a significant increase in IV was observed. For example, even though the prepolymer IV was very low (0.085 dL/g), the IV increased to as high as 2.469 dL/g at 260 °C after 48 h of SSP. Such a high IV value has never been reported in
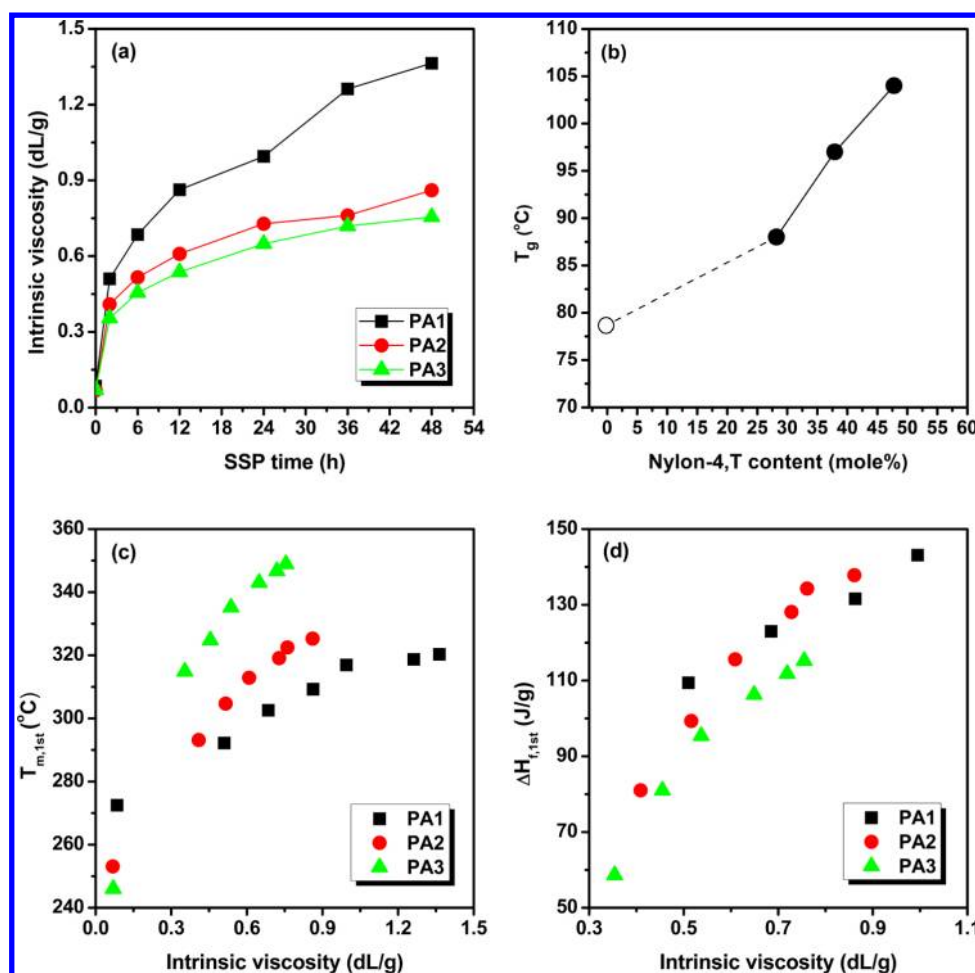
previous studies of the copolyamides of nylon-4,T/-4,6.[9,11,12] Even after 48 h of SSP, the IVs did not appear to approach asymptotic values. Furthermore, a shorter SSP time was required to reach IV values similar to those of the previous study; a value of 0.72 dL/g was obtained after 4 h of SSP at 260 °C,[9] whereas in this study, 2 h was sufficient to reach a similar IV value at the same temperature. No catalysts were used in the current or previous studies. This might imply that careful choice of SSP conditions and elimination of internal and external mass transfer can significantly enhance the SSP rate and the obtainable molecular weight. At the lower reaction temperature of 240 °C, the SSP rate decreased, as shown in Figure 5. An increase in the IVs of the polymers was still observed at 220 °C, indicating that chain extension occurred even at this low reaction temperature.

The melting behaviors of the semiaromatic polyamides as a function of SSP time at reaction temperatures of 220, 240, and 260 °C are shown in Figure S1 (Supporting Information). It can be seen from the first DSC scan that increasing either the SSP temperature or the SSP time shifted the endothermic melting peaks to higher temperatures (increased $T_{m,first}$), with concomitant sharpening of the melting isotherm and increasing of the heat of fusion (increased $\Delta H_{f,first}$). This indicates that the polymer crystals became more perfect and crystallinity increased with an increase in SSP temperature or time. Similar trends of melting points and crystallinity depending on reaction

Figure 6. Dependence of (a) $T_{m,first}$, (b) $\Delta H_{f,first}$, (c) $T_{m,second}$, and (d) $\Delta H_{f,second}$ on the intrinsic viscosities of solid-state-polymerized PA1 at 220, 240, and 260 °C.

Figure 7. Effect of nylon-4,T content on (a) intrinsic viscosity evolution during SSP and (b) T_g. Dependence of (c) $T_{m,first}$ and (d) $\Delta H_{f,first}$ on the intrinsic viscosities of the copolyamides at different nylon-4,T contents. SSP conditions: particle size = 250−500 μm, sweep-gas flow rate = 3000 mL/min, and N$_2$/steam ratio = 2:1 (v/v) at 240 °C. The T_g value of nylon-4,6 was obtained from a previous work.[6]

Table 2. Properties of the Semiaromatic Copolyamides with Different Nylon-4,T Contents Synthesized by SSP Using Prepolymers PAP1, PAP2, and PAP3 at 240 °C for 48 h

polymer	nylon-4,T content[a] (mol)		IV (dL/g)	T_g (°C)	$T_{m,first}$ (°C)	$T_{m,second}$ (°C)	$\Delta H_{f,first}$ (J/g)	$\Delta H_{f,second}$ (J/g)	$T_{d,5}$ (°C)	$T_{d,10}$ (°C)
	prepolymer	after SSP								
PA1	28.2 (PAP1)	26.3	1.364	88	320	302	146	61	390	402
PA2	37.9 (PAP2)	38.4	0.861	97	325	310	138	53	402	419
PA3	47.8 (PAP3)	49.7	0.755	104	349	314	115	12	406	423

[a]Determined by NMR analysis.

time or temperature have been observed in the SSPs of PET,[48] PTT,[18] PLA,[26] and BPA-PC.[21−23] Panels a and b of Figure 6 show the dependences of $T_{m,first}$ and $\Delta H_{f,first}$, respectively, on the IVs of the semiaromatic copolyamides synthesized at 220−260 °C. Both $T_{m,first}$ and $\Delta H_{f,first}$ increased as IV increased and reached asymptotic values in the higher-IV regime, indicating that the increase in $T_{m,first}$ is associated with the increase in the chain length of the polymer. In contrast, $T_{m,second}$ and $\Delta H_{f,second}$ of the solid-state-polymerized copolyamide samples appeared to retain similar values irrespective of the polymer molecular weight, as shown in Figure 6c,d. The values of T_m and ΔH_f did not change in additional scans. Information about $T_{m,first}$ and $\Delta H_{f,first}$ is very important in view of SSP rates[22,23,26,28] and should be applicable to the SSPs of semiaromatic copolymaide, but these values have not been reported in previous studies of the SSPs of semiaromatic copolyamides.[9−12]

3.5. Nylon-4,T Content Effects and Thermal Properties. Figure 7a shows the effect of nylon-4,T contents in the three different prepolymers (PAP1, PAP2, and PAP3; see Table 1) on the IV evolution of the semiaromatic copolyamides during SSP at 240 °C. Table 2 lists the IVs and thermal properties (T_g, T_m, and ΔH; see Figure S2 in the Supporting Information for melting isotherms) of the copolyamides after 48 h of SSP. The results clearly show that an increase in nylon-4,T content caused the SSP rate to decrease. There are at least two possible reasons for the decrease in IVs with increasing nylon-4,T content. First, the inherent reactivity of aromatic diacids is lower than that of aliphatic diacids;[9] thus, the SSP rate of the semiaromatic copolyamide with high nylon-4,T content might be expected to be lower. Second, end-group mobility could be retarded with increasing nylon-4,T content. As shown in Figures 7b and S3 (Supporting Information), T_g increased

from 88 to 104 °C as the nylon-4,T content increased from 28.2 to 47.8 mol % and was not strongly dependent on polymer molecular weight. This indicates that the T_g values of semiaromatic copolyamides are highly dependent on composition. In addition, $T_{m,first}$ of the copolyamide with the highest nylon-4,T content was much higher, as shown in Figure 7c. When the polymers with high T_g and T_m values were synthesized by SSP, the reaction temperature might not have been high enough to induce rapid chain mobility and chain extension because of higher chain stiffness.[45]

Closer inspection of Figure 7a reveals that the SSP rate of PA1 was much higher than that of PA2 or PA3, whereas the difference between the SSP rates of PA2 and PA3 was relatively small. These SSP results might be caused by the crystallinity of the solid-state-polymerized polymer. Polymer crystallinity is another important parameter that controls SSP rate by retarding chain mobility or increasing the number of end groups in the amorphous region.[2] In our previous studies of the SSPs of PTT[18] and BPA-PC,[22,23] we showed that the prepolymer with lower crystallinity always resulted in a higher-molecular-weight polymer. In this study, the crystallinity of PA3 was always lower than those of PA1 and PA2, as shown in Figure 7d. The lower crystallinity of PA3 might compensate for the retardation effect of the chain extension reaction caused by higher nylon-4,T content (e.g., lower reactivity of aromatic diacid and increased chain stiffness). This might cause the smaller difference in IV evolution between PA2 and PA3.

Analyses of COOH and NH$_2$ end-group concentrations were attempted using a titration method with various solvents (e.g., o-cresol, benzyl alcohol, m-cresol, phenol, 1,1,1,3,3,3-hexa-fluoro-2-propanol) that which have been widely used in previous studies of high-temperature polyamides.[6−9] Although the prepolymers were highly soluble in the tested solvents, the solid-state-polymerized samples either had very poor solubility or precipitated during the titration; thus, further end-group analysis was not carried out. Instead, quantification of the nylon-4,T and nylon-4,6 contents of the semiaromatic copolyamides was performed using 500 MHz ^{1}H NMR spectroscopy. Figure 8 shows ^{1}H NMR spectra and peak assignments of the PA1, PA2, and PA3 copolyamides that were solid-state-synthesized at 240 °C for 48 h. The peaks associated with nylon-4,T (i) increased and the peaks associated with nylon-4,6 (e−h) decreased with an increase in the nylon-4,T content of the prepolymer. Quantification of each component in the copolyamides was carried out using the peaks at 2.5−2.8 ppm (peaks e and h) and 7.9−8.1 ppm (peak i), and the results are listed in Table 2. The amounts of nylon-4,T in PA1, PA2, and PA3 were very similar to those in their prepolymers, suggesting that the final polymer composition can be easily controlled by adjusting the starting salt composition. Based on the total area of the diacid (TPA and AA) NMR peaks (i, e, and h) and the diamine NMR peak (a), the diacid concentration in the copolyamides was determined to be slightly higher than the diamine concentration. The amine end-group losses of PA1, PA2, and PA3 at 240 °C after 48 h of SSP were estimated to be 1.37, 1.98, and 1.97 mol %, respectively. This implies that side reactions, which often lead to the formation of dead end groups, occurred only marginally during SSP.

To assess the thermal stability of the copolyamides, TGA was performed for the prepolymers and the polymers synthesized by SSP at 240 °C for 48 h, and the results are shown in Figure 9 and Table 2. The TGA curves in Figure 9a show that, as the nylon-4,T content increased, the thermal stability of the
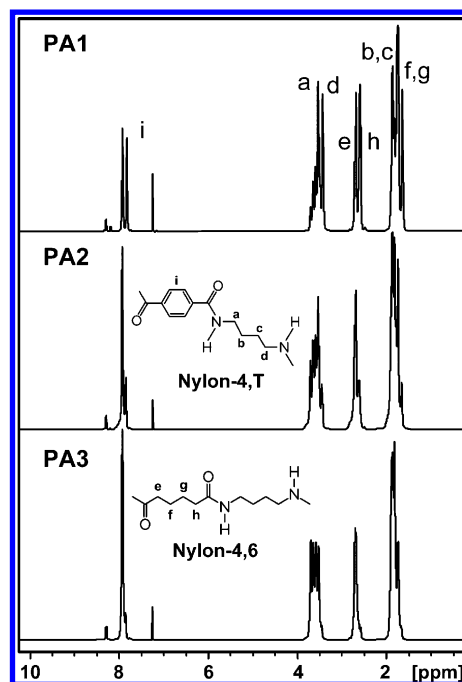

Figure 8. ^{1}H NMR spectra of PA1, PA2, and PA3 synthesized by SSP at 240 °C for 48 h.
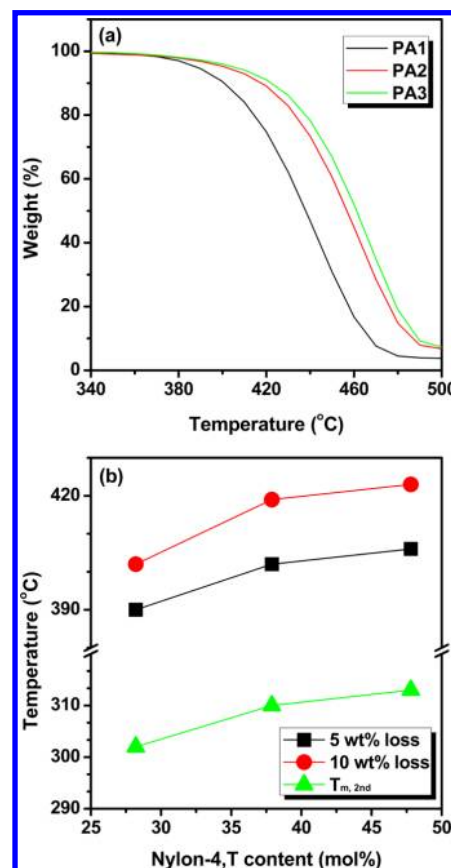

Figure 9. (a) TGA profiles and (b) $T_{m,second}$, $T_{d,5}$, and $T_{d,10}$ values of PA1, PA2, and PA3 synthesized by SSP at 240 °C for 48 h.

copolyamides improved. The values of $T_{d,5}$, and $T_{d,10}$ for the copolyamides were determined from the TGA curves and are shown in Figure 9b. For comparison, the $T_{m,second}$ values of the copolyamides are also included in the figure. As nylon-4,T

content increased from 28.2 to 47.8%, $T_{d,5}$ increased from 390 to 406 °C, and $T_{d,10}$ increased from 402 to 423 °C. These decomposition temperatures are much higher than the melting temperatures (less than 300 °C). Thus, the semiaromatic copolyamides can be melt-processed, for example, in an extruder. The $T_{d,5}$, and $T_{d,10}$ values of the solid-state-synthesized samples were not strongly dependent on their IVs, as shown in Figure S4 (Supporting Information). This indicates that the decomposition temperatures of the copolyamides are not influenced by their molecular weights after SSP, but that the nylon-4,T content is the dominant factor that determines the thermal stability.

4. CONCLUSIONS

Solid-state polymerization of semiaromatic nylon-4,T/-4,6 copolyamides was studied using prepolymers with different nylon-4,T contents (28.2, 37.9, and 47.8 mol %). SSP was carried out at reaction temperatures in the range of 220−260 °C with a mixture of N_2 and steam. Under conditions chosen to eliminate the influences of external and internal diffusion during SSP, an extremely high-molecular-weight polymer with an IV of 2.469 dL/g was produced by SSP at 260 °C for 48 h. As the nylon-4,T content increased, the SSP rate decreased because of the inherently low reactivity of the aromatic diacid and the inhibition of chain-end mobility. The copolyamides with higher nylon-4,T contents had higher glass transition, melting, and decomposition temperature than those with lower nylon-4,T contents.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

First and- second-scan DSC melting isotherms of semiaromatic polyamides solid-state-polymerized using PAP1 at 220, 240, and 260 °C. First- and second-scan DSC melting isotherms of semiaromatic polyamides solid-state-polymerized using PAP1, PAP2, and PAP3 at 240 °C. T_g values of semiaromatic copolyamides solid-state-polymerized using PAP1, PAP2, and PAP3 at 240 °C. Dependence of $T_{d,5}$, and $T_{d,10}$ of PA1 and PA2 on the intrinsic viscosity during SSP at 240 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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