

# Direct Synthesis of Thermally Stable Semiaromatic Polyamides by Bulk Polymerization Using Aromatic Diamines and Aliphatic Dicarboxylic Acids

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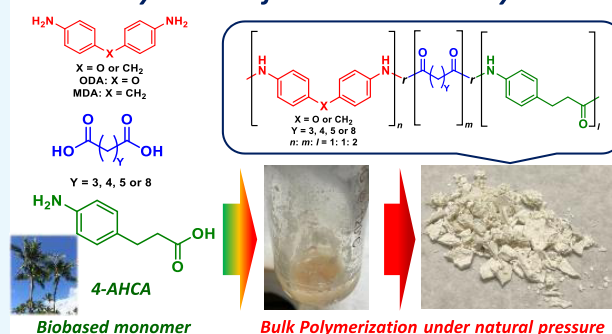
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Supporting Information

**ABSTRACT:** Semiaromatic polyamides were directly synthesized by bulk polycondensation of aliphatic dicarboxylic acids (with 5, 6, 7, and 10 carbon numbers) and aromatic diamines (4,4'-oxydianiline and 4,4'-diaminodiphenylmethane) under natural pressure. In addition, copolyamides were successfully obtained by the copolymerization of aliphatic dicarboxylic acids, aromatic diamines, and biobased amino acid, 4-aminohydrocinnamic acid. The obtained polyamides had relatively high inherent viscosity values of 0.35–0.76 dL/g. The obtained polyamides exhibited good thermal stability with  $T_{d5\%}$  in the range of 316–416 °C, even when incorporated with aliphatic methylene units. In particular, some copolyamides (2AO, 2PO, and 2GM) had high  $T_g$  values of 150, 158, and 156 °C and relatively low  $T_m$  values of 277, 288, and 234 °C, respectively, which may be preferable thermal properties for melt-drawing processes.

## Direct Synthesis of Semiaromatic Polyamides



## INTRODUCTION

Wholly aromatic polyamides (aramids) have been used as valuable superengineering plastics in the inflammable clothing, automobile, and aerospace industries because of their excellent mechanical strength and heat resistance. Unlike aliphatic polyamides (e.g., nylons) whose main chains are composed of aliphatic skeletons, aramids have aromatic main chains with hydrogen bonds that form a rigid-rod molecular framework.<sup>1–6</sup> However, due to their high heat resistance, the melting temperatures are too high, which generally makes molding and processing difficult.<sup>2,3</sup> To solve this problem, semiaromatic polyamides, which incorporate both aliphatic and aromatic components, have received much attention. They are expected to improve the processability originating from lower thermal transition temperatures than aramids while maintaining high thermal stability and mechanical properties. Although semiaromatic polyamides have such balanced properties, they generally have similar melting points and decomposition temperatures, and they sometimes decompose before being molten, which significantly limits the potential of low-cost melt processing. Although attempts have been made to decrease the melting points of semiaromatic polyamides by simply extending the aliphatic hydrocarbons in the main chains, another problem arises: their glass transition temperatures also decrease to read to inferior heat resistance.<sup>3,7</sup> Therefore, a careful molecular design that balances the two trade-off properties of thermal properties and processability is essential.

Looking at a synthetic method, polyamides are generally synthesized by solution polymerization. However, this method has disadvantages in terms of environmental friendliness, i.e., the use of acid chlorides as monomers to eliminate many salts after polymerization and the use of organic solvents.<sup>2,8–10</sup> Thus, the development of a simpler and more environmentally friendly polymerization method is required. To synthesize a semiaromatic polyamide in an environmentally friendly manner, there are two direct bulk polymerization strategies: (a) direct polymerization between an aliphatic diamine and aromatic dicarboxylic acid and (b) direct polymerization between an aromatic diamine and aliphatic dicarboxylic acid. For example, method (a), where intermediate ammonium salts can be isolated and purified, has been established based on direct bulk polymerization to afford poly(hexamethylene terephthalamide) (6T), poly(decamethylene terephthalamide) (10T), etc.<sup>11–13</sup> Meanwhile, method (b) has rarely been reported, probably due to the use of low-nucleophilic aromatic diamines that cannot form salts with carboxylic acid compounds, and strict stoichiometry control in a two-monomer ratio is required to obtain high-molecular-weight

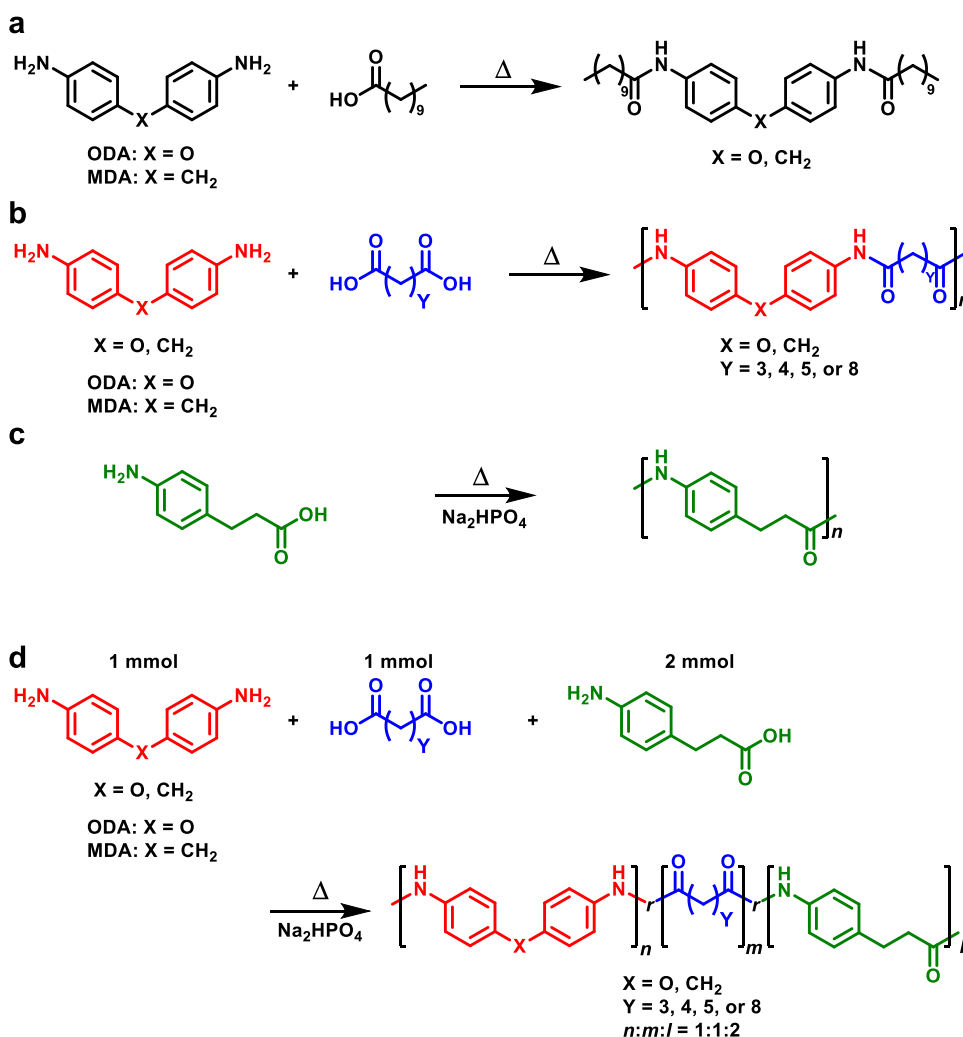
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Scheme 1. (a) Model Reaction of Aromatic Diamines (ODA and MDA) and Undecanoic Acid, (b) Polymerization of ODA and MDA and GA, AA, PA, or SA, (c) Polymerization of 4-AHCA, and (d) Copolymerization of ODA or MDA, GA, AA, PA, or SA and 4-AHCA under Bulk and Natural Pressure Conditions



polymers. In addition, the polymerization temperatures are typically much higher than those when using aliphatic diamines, which provides risks of monomer sublimation, side reactions, and/or polymer decomposition during polymerization.

Holmer et al. reported the direct synthesis of semiaromatic polyamides by bulk polymerization derived from aromatic diamines 4,4'-diaminodiphenylmethane (MDA) and aliphatic dicarboxylic acids azelaic acid, sebacic acid, and dodecanedioic acid.<sup>14</sup> However, the reported synthetic protocol is somewhat cumbersome, including the use of autoclave reactors and decompression operation processes. In addition, there is a limitation in the adoptable monomer for this system. Recently, a biobased AB-type monomer, 4-aminohydrocinnamic acid (4-AHCA), which is obtained from glucose *via* a bioprocess, was successfully bulk-polymerized in vacuo at 175 °C.<sup>15</sup> However, a systematic study on the direct synthesis of semiaromatic polyamides by bulk polymerization under natural pressure without a decompression operation process has never been reported.

Ueda and co-workers reported the direct synthesis of aramids by bulk polycondensation under natural pressure.<sup>16–19</sup> By carefully adjusting the polymerization temperature/time in

three or four steps, they successfully synthesized high-molecular-weight aramids. In this study, we report the results of the direct synthesis of semiaromatic polyamides derived from aromatic diamines and aliphatic dicarboxylic acids by bulk polymerization under natural pressure according to Ueda's approach, where we adjusted the polymerization temperature/time in three or four steps. In practice, 4,4'-oxydianiline (ODA) and MDA with high boiling points (b.p. > 300 °C) are employed as aromatic diamines. Glutaric acid (GA), adipic acid (AA), pimelic acid (PA), and sebacic acid (SA) are employed as aliphatic dicarboxylic acids. The effect of their carbon numbers (C<sub>5</sub>–C<sub>7</sub>, C<sub>10</sub>) on thermal properties was investigated in detail. Furthermore, an aromatic amine, aliphatic dicarboxylic acid, and biobased 4-AHCA were copolymerized to increase the composition of such a biobased material, which makes it accessible to a more environmentally friendly system.

## RESULTS AND DISCUSSION

**Model Reaction.** Prior to the synthesis of semiaromatic polyamides, a model reaction was performed to check whether the reaction could proceed with aromatic diamines (ODA and MDA) and aliphatic monocarboxylic acid

Table 1. Results of Polymerization and Thermal Properties

entry	X	Y	condition T/t [°C/h]			yield [%]	$\eta_{inh}^a$ [dL/g]	$T_{d5\%}$ [°C]	$T_g^b$ [°C]	$T_m^b$ [°C]	$T_c^b$ [°C]	
GO	O	3	100/1.0	200/2.0	290/7.0	59	0.35	363	N/A	N/A	N/A	
AO	O	4	200/1.0	210/2.0	300/7.0	92	0.76	388	280	N/A	N/A	
PO	O	5	110/1.0	200/2.0	300/7.0	78	0.63	382	230	N/A	N/A	
SO	O	8	150/1.0	210/2.0	270/7.0	78	0.35	376	185	N/A	N/A	
GM	CH <sub>2</sub>	3	100/1.0	200/2.0	270/7.0	95	0.39	323	N/A	N/A	N/A	
AM	CH <sub>2</sub>	4	100/1.0	200/2.0	250/7.0	97	0.41	316	N/A	230	220	
PM	CH <sub>2</sub>	5	110/1.0	200/2.0	250/9.0	94	0.62	391	152	N/A	N/A	
SM	CH <sub>2</sub>	8	100/1.0	200/2.0	250/7.0	95	0.47	416	125	255	195	
P-4AHCA1			200/1.0	210/2.0	300/7.0	94	0.33	364	N/A	N/A	N/A	
P-4AHCA2 <sup>c</sup>			200/1.0	210/2.0	300/7.0	93	0.36	376	N/A	N/A	N/A	
2GO <sup>c</sup>	O	3	100/1.0	200/2.0	250/2.0	300/5.0	91	0.23	333	138	N/A	N/A
2AO <sup>c</sup>	O	4	200/1.0	210/2.0	300/7.0		70	0.21	383	150	277	248
2PO <sup>c</sup>	O	5	110/1.0	200/2.0	300/7.0		94	0.57	405	158	288	250
2SO <sup>c</sup>	O	8	200/1.0	210/2.0	250/7.0		95	0.53	408	189	N/A	N/A
2GM <sup>c</sup>	CH <sub>2</sub>	3	100/1.0	200/2.0	250/2.0	270/5.0	98	0.20	390	156	234	197
2AM <sup>c</sup>	CH <sub>2</sub>	4	100/1.0	200/2.0	250/2.0	280/5.0	84	0.23	340	152	N/A	199
2PM <sup>c</sup>	CH <sub>2</sub>	5	110/1.0	200/2.0	250/9.0		98	0.37	375	163	N/A	197
2SM <sup>c</sup>	CH <sub>2</sub>	8	100/1.0	200/2.0	250/7.0		89	0.36	402	145	N/A	N/A

<sup>a</sup> $\eta_{inh}$  was measured at 30 °C in conc. H<sub>2</sub>SO<sub>4</sub> or N,N-dimethylformamide (DMF) at a concentration of 0.5 g/dL. <sup>b</sup>DSC: 10 °C/min. <sup>c</sup>1 wt % Na<sub>2</sub>HPO<sub>4</sub> was added as an antioxidant in the polymerization.

(undecanoic acid) (Scheme 1a) at 200 °C for 2 h under solvent-free and natural pressure conditions in a sealed heat/pressure-resistant tube after nitrogen purging. A small excess of undecanoic acid toward an amino group of aromatic diamines was used. The reaction proceeded while maintaining a molten state with a yellow to brown color. After cooling to room temperature, the objective N,N'-(oxybis(4,1-phenylene))-diundecanamide and N,N'-(methylenebis(4,1-phenylene))-diundecanamide were obtained with yields of 98 and 94%, respectively. The FTIR spectra of both products show absorption peaks assignable to the amide groups. In addition, their chemical structures coincided with the targeted structures, as confirmed by <sup>1</sup>H NMR (Figures S1–S6). Thus, the model reaction of the aromatic amines and aliphatic undecanoic acid proceeded without side reactions in a molten state at 200 °C under solvent-free and natural pressure conditions.

**Synthesis of Semiaromatic Polyamides by Direct Bulk Polymerization of Aromatic Diamines and Aliphatic Dicarboxylic Acids.** In bulk polycondensation using ODA and aliphatic dicarboxylic acids as monomers, the thermal decomposition of products is more dominant than the polymerization reaction.<sup>14</sup> Meanwhile, the employment of MDA instead of ODA led to successful melt polymerization by choosing appropriate dicarboxylic acids such as azelaic acid, sebacic acid, and dodecanedioic acid, which have long alkyl spacer units. In practice, the polymerization temperature was stepwise increased at approximately the melting point of the monomer. Then, oligomerization and polymerization continuously occurred to gradually increase the molecular weight of the polymer, which suppressed the sublimation and thermal decomposition of the products.

Based on the model reaction, the polymerization of aromatic diamines (ODA and MDA) and aliphatic dicarboxylic acids (GA, AA, PA, and SA) was performed under solvent-free and natural pressure conditions after nitrogen purging (Scheme 1b). To gradually increase the molecular weight of polyamides suppressing the side reactions, the polymerization conditions were set in three stages. The results of the polymerization are

shown in Table 1. The temperature in the third step was set below the boiling points of the dicarboxylic acids (maximum 300 °C). All of the first step reactions proceeded in a molten state at 100–200 °C and changed to the solid-phase state within approximately 30 min. Thereafter, the reaction proceeded in a solid-phase state until the end of the reaction. After polymerization, the product was dissolved in concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and poured into a large amount of a sodium bicarbonate (NaHCO<sub>3</sub>) aqueous solution to neutralize and precipitate the polymer, followed by drying in vacuo at 120 °C for 6 h. The yields were generally high in the range of 59–98%. In particular, excellent yields of 94–97% are determined for polyamides with X = CH<sub>2</sub>, probably due to the suppressed sublimation/decomposition of monomers under lower final polymerization temperature below 270 °C, compared to polyamides with X = O (final polymerization temperature: 270–300 °C). All FTIR spectra of the obtained polyamides show specific peaks at approximately 1650 cm<sup>-1</sup> assignable to amide-I groups and at approximately 3300 cm<sup>-1</sup> assignable to N–H groups (Figures S7 and S8), which indicates the progress of polymerization generating amide units. The obtained polyamides show relatively high inherent viscosity ( $\eta_{inh}$ ) values of 0.35–0.76 dL/g, which indicates that the direct bulk polymerization of aromatic diamines (ODA and MDA) and aliphatic dicarboxylic acids (GA, AA, and SA) is successful by gradually elevating the temperature in three stages under natural pressure.

**Synthesis of Semiaromatic Polyamides by Direct Bulk Polymerization of 4-AHCA.** As mentioned in the introduction, a biobased AB-type monomer 4-AHCA has been utilized for direct bulk polymerization in vacuo.<sup>15</sup> However, trials under natural pressure have never been done. In this section, the direct homopolymerization of 4-AHCA under natural pressure was investigated by similar protocols that we propose in the preceding section. The temperature/time conditions were set at 200 °C/1.0 h, 210 °C/2.0 h, and 300 °C/7.0 h (Scheme 1c). The polymerization was similar to that of ODA and aliphatic dicarboxylic acids; in the molten state in the first step, the polymerization was changed to the

solid state within 30 min and maintained in the solid state in the second and third steps. After the polymerization was completed, the product (**P-4AHCA1**) was obtained as white fibrous solids. However, its  $\eta_{\text{inh}}$  value was moderate, as determined to be 0.33 dL/g. By adding 1 wt % sodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ ) to the polymerization media as a catalyst,<sup>15</sup> the  $\eta_{\text{inh}}$  value of the product (**P-4AHCA2**) was slightly improved to 0.36 dL/g. The Fourier transform infrared spectroscopy (FTIR) spectrum of **P-4AHCA2** confirmed the existence of amide groups, which indicates the successful direct polymerization of a biobased 4-AHCA (Figure S9).

**Synthesis of Semiaromatic Copolyamides by Direct Bulk Polymerization of Aromatic Diamines, Aliphatic Dicarboxylic Acids, and 4-AHCA.** Based on the successful results of homopolyamides derived from AA + BB-type monomers and AB-type monomer (4-AHCA), the copolymerization of aromatic diamines, aliphatic dicarboxylic acids, and 4-AHCA was investigated (Scheme 1d). The polymerization results are also shown in Table 1. The polymerization temperature/time was carefully set in three or four stages. When dicarboxylic acid monomers with  $Y = 3$  and  $4$  were used, the polymerization media changed from a molten to solid phase and maintained the solid phase even after the temperature was increased to 270–300 °C, independent of  $X = \text{O}$  or  $\text{CH}_2$ . In sharp contrast, in the case of  $Y = 5$  and  $8$ , a different phenomenon was observed. When the temperature was increased up to the final stage, the melting state continued for 3–4 h and finally changed to the solid state. As a result, **2PO** ( $Y = 5$ ), **2SO** ( $Y = 8$ ), **2PM** ( $Y = 5$ ), and **2SM** ( $Y = 8$ ) showed higher  $\eta_{\text{inh}}$  values of 0.36–0.57 dL/g than other copolyamides (0.20–0.23 dL/g). It is considered that the use of monomers with long alkyl spacers decreases the  $T_m$  values of the propagating polymer chains during polymerization, which maintains a molten state for a long time to increase the viscosity of the resulting products. For all samples, the progress of polymerization was confirmed by FTIR (Figures S10 and S11). To confirm the composition of MDA/4-AHCA/GA incorporated in the resulting polyamide,  $^1\text{H}$  NMR measurement of **2GM** was performed in deuterated DMF ( $\text{DMF-}d_7$ ), which is only one soluble sample in DMF in all runs (Figure S12). As a result, the measured composition of MDA/4-AHCA/GA (26:48:26, by mol.) in **2GM** is in good agreement with that calculated (25:50:25, by mol.) based on the comonomer feed ratio. Therefore, the reactivity of the functional groups of amino and carboxylic acid in MDA, 4-AHCA, and GA seems to be similar.

**Thermal Properties.** The thermal properties of the resulting polyamides were examined by thermogravimetry (TGA) and differential scanning calorimetry (DSC) (Table 1). The TGA and DSC curves of the polyamides are shown in Figures S13–S22. All polyamides show high thermal stability and 5% weight loss temperature ( $T_{d5\%}$ ) values in the range of 316–416 °C despite being incorporated with aliphatic methylene segments. Polyamides with longer alkyl chains ( $Y = 5$  and  $8$ ) tend to show even higher  $T_{d5\%}$  values (375–416 °C) than those with shorter alkyl chains ( $Y = 3$  and  $4$ ) ( $T_{d5\%} = 316$ – $390$  °C), probably due to higher  $\eta_{\text{inh}}$  values (0.35–0.63 dL/g) for  $Y = 5$  and  $8$  than those (0.20–0.41 dL/g) for  $Y = 3$  and  $4$ , except for **AO** (0.76 dL/g). We speculate that oligomers and polymers with longer alkyl chains may be more easily mobile even in solid-state polymerization under the final temperature/time conditions, which resulted in the formation of higher-molecular-weight polymers than those with shorter

alkyl chains. We could not find distinct differences in  $T_{d5\%}$  values between ODA-based polyamides and MDA-based polyamides. FTIR spectra of **SO** before and after TGA measurement are representatively shown in Figure S23. The disappearance of N–H, C–H, and C=O (amide-I) absorptions after operating TGA confirmed the decomposition of the amide linkage of the main chains.

Meanwhile, there is a clear tendency of decreasing  $T_g$  values of homopolyamides from 280, 230, and to 185 °C by increasing  $Y$  for **AO** ( $Y = 4$ ), **PO** ( $Y = 5$ ), and **SO** ( $Y = 8$ ) and from 152 to 125 °C by increasing  $Y$  for **PM** ( $Y = 5$ ) and **SM** ( $Y = 8$ ). This is probably due to the extension of methylene units to enhance the plasticity of polyamides. In contrast, a series of copolyamides show similar  $T_g$  values for all runs at approximately 138–189 °C. Indeed, the statistical incorporation of 50 mol% 4-AHCA monomer units in ODA-based copolyimides resulted in significantly decreased  $T_g$  values, especially for polyamides with shorter  $Y = 4$  and  $5$ . For example,  $T_g$  values of **2AO** (150 °C)/**AO** (280 °C) and **2PO** (158 °C)/**PO** (230 °C) are found. This is probably because of the improved plasticity originating from statistical monomer sequences in copolyamides. However, a higher  $T_g$  value is determined for **2SO** (189 °C) than for **SO** (185 °C). This is because the 4-AHCA comonomer has the same ratio (2/1) of the aliphatic/aromatic carbon number as **AO** ( $Y = 4$ ), which shows a quite high  $T_g$  value of 280 °C and thereby increases the rigidity of copolyimide compared to **SO**. A similar tendency is observed in MDA-based copolyimides. The  $T_g$  values are newly observed for **2GM** (156 °C) and **2AM** (152 °C), although  $T_g$  values are not observed for **GM** and **AM**, probably due to the plasticization effect of copolymerization. Since the 4-AHCA comonomer has the same ratio (2/1) of the aliphatic/aromatic carbon number as **GM** ( $Y = 3$ ), higher  $T_g$  values of **2PM** (163 °C,  $Y = 5$ ) and **2SM** (145 °C,  $Y = 8$ ) than those of **PM** (152 °C,  $Y = 5$ ) and **SM** (125 °C,  $Y = 8$ ) are obtained.

Although there is no clear trend in the  $T_m$  observations for all runs, some polyamide samples show relatively low  $T_m$  values at approximately 234–288 °C, which might be preferable thermal properties for melt-drawing processes. Especially by copolymerization, high  $T_g$  values of **2AO**, **2PO**, and **2GM** are found at 150, 158, and 156 °C, whereas low  $T_m$  values are found at 277, 288, and 234 °C. Previous semiaromatic polyamides show much higher  $T_m$  values, e.g., **6T** ( $T_g = 140$  °C,  $T_m = 370$  °C)<sup>3,20</sup> and **10T** ( $T_g = 132$  °C,  $T_m = 313$  °C).<sup>21</sup> This is probably due to the existence of flexible ether (–O–) or methylene (–CH<sub>2</sub>)– linkages in aromatic amines with methylene long spacer units in dicarboxylic acids for the semiaromatic polyamide and copolyimide samples prepared in this study.

## CONCLUSIONS

In this study, we investigated the direct synthesis of semiaromatic polyamides or copolyamides by bulk polymerization of aromatic diamines and aliphatic dicarboxylic acids or bulk copolymerization of those and a biobased amino acid, 4-AHCA, under natural pressure. The polymerization temperature was carefully and stepwise set to optimize the viscosity of a concentrated  $\text{H}_2\text{SO}_4$  solution of the resulting polymers. As a result, a high  $\eta_{\text{inh}}$  value of 0.76 dL/g was achieved for **AO**. The obtained polyamides and copolyamides showed high thermal stability in the range of  $T_{d5\%} = 316$ – $416$  °C despite the incorporation of aliphatic units. By copolymerization, high  $T_g$

values of **2AO**, **2PO**, and **2GM** are found at 150, 158, and 156 °C, whereas low  $T_m$  values are found at 277, 288, and 234 °C, which may be preferable thermal properties for the melt-drawing process. The proposed direct bulk polymerization method to synthesize semiaromatic polyamides provides a low environmental impact and can be applied to the large-scale synthesis of heat-resistant resins.

## EXPERIMENTAL SECTION

**Materials.** Undecanoic acid (>99%), ODA (>98%), MDA (>98%), AA, (>99%), GA (>99%), PA (>98%), SA (>98%), and 4-AHCA (>98%) were purchased from Tokyo Chemical Industry Co., Ltd. ODA and MDA were purified by recrystallization with ethanol and toluene, respectively.  $H_2SO_4$  (>95%) was purchased from Kanto Chemical Co., Ltd.  $Na_2HPO_4$  was purchased from FUJIFILM Wako Pure Chemical Co., Ltd. *N,N*-Dimethylacetamide (DMAc, >99.8%) was purchased from Sigma-Aldrich, Japan.

**Measurements and Characterization.**  $^1H$  nuclear magnetic resonance ( $^1H$  NMR) spectra were recorded on a JEOL JNM-ECX400 spectrometer at resonant frequencies of 400 MHz in deuterated dimethyl sulfoxide ( $DMSO-d_6$ ) at 50 °C,  $DMF-d_7$  at room temperature, or on a JEOL JNM-ECZ600/ M1 spectrometer at resonant frequencies of 600 MHz in  $DMF-d_7$  at 90 °C.  $^{13}C$  NMR was recorded on a JEOL JNM-ECZ600/M1 spectrometer at resonant frequencies of 150 MHz in  $DMF-d_7$  at 90 °C. The logarithmic viscosity method was employed to measure the viscosity using an Ostwald viscometer and a thermostatic bath (TV-5S, Thomas Kagaku Co., Ltd.). The samples were dissolved in concentrated  $H_2SO_4$  and adjusted to 0.5 dL/g, and the flow time was measured at 30 °C. FTIR spectra were measured using a Thermo Fisher Scientific Nicolet iS5 FTIR with the sample ground. TG/DTA 6300 and DSC 6200 were used for thermal characterization. TGA was performed by placing an aluminum pan containing a sample (<10 mg) on a balance in a weighing chamber. The heating rate was set to 10 °C/min; the scan started at room temperature and ended at 550 °C, followed by holding for 10 min. For DSC measurements, the maximum temperature was set at approximately 20 °C below the 1% weight loss temperature obtained by TGA of the same sample. The heating and cooling rates were set to 10 °C/min, and the 1st cooling scan and 2nd heating scan were taken to determine the  $T_c$  and  $T_g/T_m$  values, respectively.

**Model Reaction.** Undecanoic acid (3.00 mmol) and ODA or MDA (1.00 mmol) were placed in a pressure-resistant tube, which was filled with nitrogen and tightly closed with a screw cap. The tube was placed in an electric furnace, and the temperature was increased to 200 °C and allowed to stand for 2 h. The reaction product was dissolved in DMAc (10 mL) and poured into a 3%  $NaHCO_3$  aq. solution. The precipitates were collected by suctional filtration and vacuum dried at 120 °C for 6 h to afford the reaction products.

**General Synthesis of Polyamides by Bulk Polymerization.** Dicarboxylic acid ( $Y = 3, 4, 5,$  and  $8, 2.00$  mmol) and aromatic diamine (2.00 mmol) were placed in a pressure-resistant tube, which was filled with nitrogen and tightly closed with a screw cap. The tube was placed in an electric furnace, and the temperature was increased stepwise at the set temperature/time. After the bulk polymerization was completed, the sample was cooled to room temperature and dissolved in concentrated  $H_2SO_4$ . The solution was slowly poured into  $NaHCO_3$  aq. with a water bath to precipitate the

polymer. It was collected by suctional filtration, followed by washing with water/methanol (3:2, by vol., 500 mL) in a beaker, and again collected by suctional filtration. Finally, it was dried in a vacuum at 120 °C for 6 h to afford the semiaromatic polyamides.

**General Procedure to Synthesize Polyamide with 4-AHCA by Bulk Polymerization.** 4-AHCA (0.500 g, 3.00 mmol) with or without  $Na_2HPO_4$  (1.0 wt %) was prepared in a pressure-resistant tube and tightly sealed with a screw cap. The pressure-resistant tube was placed in an electric furnace, and the temperature was stepwise increased as follows: 200 °C/1 h, 210 °C/2 h, and 300 °C/7 h. After the bulk polymerization was completed, the sample was cooled to room temperature and dissolved in concentrated  $H_2SO_4$ . The solution was slowly poured into  $NaHCO_3$  aq. with a water bath to precipitate the polymer. It was collected by suctional filtration, washed with water/methanol (3:2, by vol., 500 mL) in a beaker, and again collected by suctional filtration. Finally, it was dried in a vacuum at 120 °C for 6 h to afford polyamides based on 4-AHCA.

**General Procedure to Synthesize Copolyimides by Bulk Polymerization.** 4-AHCA (0.500 g, 3.00 mmol), aromatic diamine (1.00 mmol), dicarboxylic acid ( $Y = 3, 4, 5,$  and  $8, 1.00$  mmol), and  $Na_2HPO_4$  (1.0 wt %) were prepared in a pressure-resistant tube and tightly sealed with a screw cap. The pressure-resistant tube was placed in an electric furnace, and the temperature was stepwise increased at the set temperature/time. After the bulk polymerization was completed, the sample was cooled to room temperature and dissolved in concentrated  $H_2SO_4$ . The solution was slowly poured into  $NaHCO_3$  aq. with a water bath to precipitate the polymer. It was collected by suctional filtration, washed with water/methanol (3:2, by vol., 500 mL) in a beaker, and again collected by suctional filtration. Finally, it was dried in a vacuum at 120 °C for 6 h to afford the semiaromatic copolyamides.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c06983>.

Experimental details of the model reaction, FTIR and  $^1H/^{13}C$  NMR spectra of the products obtained by the model reaction, polymer synthesis, FTIR spectra of studied polymers,  $^1H$  NMR spectrum of the representative polymer prepared, TGA and DSC thermograms of studied polymers, and FTIR spectra of the representative polymers before and after TGA measurement (PDF)

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## Notes

The authors declare no competing financial interest.

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