Divergent Process for C<sub>10</sub>, C<sub>11</sub> and C<sub>12</sub> ω-Amino Acid and α,ω-Dicarboxylic Acid Monomers of Polyamides from Castor Oil as a Renewable Resource

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Polyamides have great potentials for diverse applications and the present production of their monomers mostly relies on resources from fossil fuel. Starting from undecylenic acid, a natural resource, we have developed both divergent and efficient processes for C<sub>10</sub>, C<sub>11</sub> and C<sub>12</sub> ω-amino acid and α,ω-dicarboxylic acid monomers of the polyamides.

Key Words : Castor oil, Divergent process, α,ω-Dicarboxylic acids, ω-Aminoacids, Monomers of thermostatic elastomers (TPEs)

Introduction

Petrochemical industries have emitted huge amount of carbon dioxide and caused environmental problems such as climate change. In addition, fossil fuels are limited resource and they will be depleted in the near future as their demands increase. Thus, petroleum-based industries are facing challenges in technical, economic and environmental issues and the call for alternative carbon sources is growing. As a result, replacement of fossil fuel-based raw materials with renewable natural resources is a major concern from both economic and environmental perspectives. Biomass, which is biological material from living organisms such as corn starch, sugarcane and vegetable oil, has emerged as an important alternative resource because it has superior advantages over fossil fuel; it is economic, renewable, flexible and environmentally friendly. Currently, about 3% of the global chemicals market sales are made up of “green chemicals” and the market share would grow to about 25% of global chemicals sales by 2025. In addition, consumer interests in green products and public policy are accelerating the growth of green chemicals in the marketplace.

Among the green chemicals, bioplastics (green plastics) derived from sustainable biomass are predicted to show the highest growth rate due to their wide range of applications. Especially, extensive research and development on thermoplastic elastomers (TPEs) have been conducted because TPEs typically have advantages of both plastic and rubbery materials as well as their superior qualities to either rubbers or plastics. Synthetic polyamides among the TPEs have been utilized in engineering plastics and the demands for the production are increasing due to their high strength, toughness, and thermal stability. Polyamides have also great potentials for other functional applications, particularly in biomedical fields as they show good biocompatibility and degradability.

Since most of their monomers have been obtained from non-renewable resources such as natural gas and petroleum, a lot of research has been conducted to obtain their monomers from alternative sources such as vegetable oil. Vegetable oil can be an ideal alternative source because it is abundant throughout the world, and moreover, can be easily modified to the polymer precursors due to its active chemical sites such as double bonds and esters. However, only a few processes are successfully commercialized for polyamide monomers. Current processes require various sources of biomass for the production of the polyamide monomers having different chain length. For example, a C<sub>9</sub> ω-amino acid has been obtained from olive oil and both C<sub>10</sub> and C<sub>11</sub> ω-amino acids from castor oil. Vernonia oil was used to give both C<sub>11</sub> and C<sub>12</sub> ω-amino acids. To improve the efficiency of the production, we have designed a new process to obtain various polyamide monomers having different chain length from one natural resource, castor oil (Figure 1).

Experimental

Materials were obtained from commercial suppliers and were used without further purification. The reactions were monitored with SiO<sub>2</sub> TLC plates under UV light (254 nm) followed by visualization with a phosphomolybdic acid or...
a ninhydrin stain solution. Column chromatography was performed on silica gel 60 (70-230 mesh). Infrared (IR) spectra were recorded on a JASCO FT-IR 200. Films for IR were spin-coated on silicon wafers. 1H NMR spectra were measured on JEOL 300 MHz or Bruker 400 MHz while 13C NMR spectra were measured on JEOL 75 MHz or Bruker 100 MHz. Tetramethylsilane was used as an internal reference (0.0 ppm): chemical shift (multiplicity, coupling constant in Hz, integration). Melting points were determined with an open capillary melting point apparatus and were uncorrected. High resolution mass spectra were obtained with a JEOL JMS-AX505WA mass spectrometer.

Decanedioic Acid (3). A solution of undecylenic acid 1 (3.0 g, 14.8 mmol) in dichloromethane (100 mL) and methanol (50 mL) was cooled to −78 °C, and a stream of ozone was bubbled into the reaction mixture until a light blue color became evident. Argon was then bubbled through the reaction mixture until the blue color disappeared and then was added 1 N aqueous NaHCO3 solution (44.4 mL, 44.4 mmol). The reaction mixture was stirred at room temperature for 6 h. The solvent was evaporated and washed with diethyl ether (50 mL × 2). The aqueous layer was acidified by 6 N aqueous hydrochloric acid (7.5 mL) and extracted with ethyl acetate (50 mL × 3). The combined organic extracts were dried over MgSO4, filtered and concentrated in vacuo. Decanedioic acid 3 (3.00 g, quantitative) was obtained as a white solid after recrystallization in water. mp 131 °C [lit. 131-132 °C]; 1H NMR (400 MHz, DMSO-d6) δ 11.99 (br s, 2H), 2.19-2.17 (m, 4H), 1.64-1.57 (m, 2H), 1.39-1.28 (m, 10H); 13C NMR (100 MHz, DMSO-d6) δ 174.9, 34.1, 29.1, 27.3, 24.9; HRMS (CI) calcd for C16H16O4 [M + H]+ 201.1492, found 201.1491.

Methyl 10-(Benzyllamino)decanoate (5). To a solution of aldehyde 4 (355 mg, 1.77 mmol) in distilled methanol (10 mL) was added benzylamine (1.0 mL, 9.14 mmol) under nitrogen atmosphere and the reaction mixture was stirred for 1 h at room temperature. To the reaction mixture was added 10 wt % palladium on carbon (18.0 mg, 0.018 mmol). The reaction mixture was stirred for 8 h under 40 bar of hydrogen atmosphere and the resulting mixture was filtered through a celite pad with excess methanol. The filtrate was concentrated in vacuo. Purification by silica gel column chromatography (1.20 v/v, MeOH:CH2Cl2) afforded methyl 10-(benzylamino)decanoate (5) (414 mg, 81%) as a colorless liquid; IR (coated on silicon wafer) 3325, 1738, 1199, 1172 cm−1; 1H NMR (400 MHz, CDCl3) δ 7.32-7.25 (m, 5H), 3.78 (s, 2H), 3.66 (s, 3H), 2.62 (t, J = 7.3, 2H), 2.29 (t, J = 7.6, 2H), 1.64-1.55 (m, 2H), 1.53-1.42 (m, 2H), 1.35-1.24 (m, 11H); 13C NMR (100 MHz, CDCl3) δ 174.3, 140.4, 128.4, 128.1, 126.9, 54.0, 51.4, 49.4, 34.1, 30.0, 29.4, 29.2, 29.1, 27.3, 24.9; HRMS (CI) calcd for C18H20NO2 [M + H]+ 292.2277, found 292.2279.

Methyl 10-((tert-Butoxycarbonylamino)decanoate (6). To a solution of 7 (520 mg, 1.78 mmol) in methanol (25 mL) was added 20 wt % palladium hydroxide on carbon (52.0 mg, 0.074 mmol). The reaction mixture was stirred for 10 h at 50 °C under 50 bar of hydrogen atmosphere and then filtered through a celite pad with excess methanol. The filtrate was concentrated in vacuo to give the free amine as a crude product. Di-(tert-butyl) dicarbonate (0.46 mL, 2.14 mmol) was added to a solution of the crude free amine in methanol (5.0 mL) and the reaction mixture was stirred for 30 min and concentrated in vacuo. Purification by silica gel column chromatography (1.4 v/v, EtOAc:hexane) afforded methyl 10-((tert-butoxycarbonylamino)decanoate 6 (529 mg, 99%) as a white solid. mp 44 °C; IR (coated on silicon wafer) 3385, 1732, 1690, 1516, 1168 cm−1; 1H NMR (400 MHz, CDCl3) δ 4.49 (br s, 1H), 3.67 (s, 3H), 3.09 (app. q, J = 6.4, 2H), 2.30 (t, J = 7.6, 2H), 1.63-1.58 (m, 2H), 1.50-1.40 (m, 11H), 1.26-1.34 (m, 10H); 13C NMR (100 MHz, CDCl3) δ 174.3, 156.0, 85.2, 51.4, 40.6, 34.1, 30.0, 29.3, 29.2, 29.1, 28.4, 26.8, 24.9; HRMS (CI) calcd for C18H20NO2 [M + H]+ 302.2331, found 302.2332.

10-Aminodecanedioic Acid Hydrochloride Salt (7). A mixture of conc. aqueous hydrochloric acid (5.0 mL) and the Boc-protected amino ester 6 (474 mg, 1.57 mmol) was heated under reflux for 2.5 h. The resulting reaction mixture was concentrated in vacuo and dissolved in hot water. The
resulting solution was filtered and rinsed with hot water. The combined filtrate was concentrated in vacuo to afford 10-
aminoacetoic acid hydrochloride salt 7 (344 mg, 98%) as a white solid. mp 156.8-157.2 °C [lit. 157-159°C]11; IR (coated on silicon wafer) 3206-2974 (br), 1725, 1583 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 11.99 (br s, 1H), 7.84 (br s, 3H), 2.80-2.70 (m, 2H), 2.19 (t, J = 7.4, 2H), 1.58-1.44 (m, 4H), 1.34-1.22 (m, 10H); ¹³C NMR (100 MHz, DMSO-d₆) δ 174.9, 39.2, 34.1, 29.1, 29.0, 28.9, 27.3, 26.3, 24.9; HRMS (Cl) calcd for C₁₀H₁₇NO₂ [M - Cl]⁺ 188.1651, found 188.1647.

**Methyl 11-Nitroundec-10-enoate (8).** A mixture of nitromethane (4.0 mL, 73.8 mmol) and aldehyde 4 (1.08 g, 5.39 mmol) was stirred at 0 °C. Sodium hydroxide (237 mg, 5.93 mmol) was added slowly. The reaction mixture was stirred at room temperature for 1.5 h. The mixture was diluted with diethyl ether (30 mL) and washed with an aqueous solution of saturated NH₄Cl (30 mL × 2), and brine (30 mL × 2). The organic layer was dried over MgSO₄, filtered, and concentrated in vacuo. Purification by silica gel column chromatography (1:4 v/v, EtOAc:hexane) afforded the nitroalcohol intermediate (1.38 g, 98%) as a light yellowish solid. mp 56-57 °C; IR (coated on silicon wafer) 3426, 2925, 1722, 1557, 1357 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 4.46-4.31 (m, 3H), 3.67 (s, 3H), 2.55-2.52 (m, 1H), 2.31 (t, J = 7.5, 2H), 1.64-1.58 (m, 2H), 1.51-1.47 (m, 2H), 1.39-1.31 (m, 10H); ¹³C NMR (75 MHz, CDCl₃) δ 174.4, 80.6, 68.6, 51.5, 34.1, 33.6, 29.2, 29.1, 29.0, 25.1, 24.9; HRMS (Cl) calcd for C₁₀H₁₇NO₂ [M + H]⁺ 242.1654, found 242.1656.

To a solution of the nitroalcohol intermediate (1.19 g, 4.55 mmol) in dichloromethane (10 mL) was added triethylamine (0.46 mL, 5.92 mmol) at 0 °C, and then methanesulfonyl chloride (1.6 mL, 11.4 mmol) was added dropwise. The resulting mixture was stirred for 10 min at room temperature and then was diluted with diethyl ether (50 mL) and washed with an aqueous solution of saturated NH₄Cl (30 mL × 2), and then with brine (30 mL × 2). The organic layer was dried over MgSO₄, filtered, and concentrated in vacuo. Purification by silica gel column chromatography (1:4 v/v, EtOAc:hexane) afforded nitroalkene 8 (1.09 g, 98%) as a pale yellow liquid: IR (coated on silicon wafer) 1738, 1554, 1377 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 4.38 (t, J = 7.1, 2H), 3.67 (s, 3H), 2.30 (t, J = 7.5, 2H), 2.05-1.96 (m, 2H), 1.64-1.59 (m, 2H), 1.34-1.28 (m, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 174.3, 75.7, 51.5, 34.1, 29.2, 29.1, 28.7, 27.4, 26.2, 24.9; HRMS (Cl) calcd for C₁₁H₁₇NO₂ [M + H]⁺ 246.1705, found 246.1703.

**Undecanedioic Acid (10).** A solution of nitroalkane 9 (66.0 mg, 0.27 mmol) in conc. aqueous hydrochloric acid (10 mL) was heated under reflux for 4 h and then concentration of the reaction mixture in vacuo afforded undecanedioic acid 10 (46.0 mg, 79%) as a white solid after recrystallization in water. mp 99-102 °C [lit. 131-132 °C]12; IR (coated on silicon wafer) 1696 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 11.99 (br s, 2H), 2.19 (t, J = 7.4, 4H), 1.50-1.46 (m, 4H), 1.29-1.22 (m, 10H); ¹³C NMR (100 MHz, DMSO-d₆) δ 173.8, 33.3, 28.6, 28.6, 24.6; HRMS (Cl) calcd for C₁₁H₁₄O₄ [M + H]⁺ 217.1440, found 217.1443.

**11-Aminoundecanoic Acid Hydrochloride Salt (11).** To a solution of nitroolefin 8 (680 mg, 2.78 mmol) in ethyl acetate (3 mL) was added 10 wt % palladium on carbon (68.0 mg, 0.063 mmol). The reaction mixture was stirred for 10 h at room temperature under 25 bar of hydrogen atmosphere and then filtered through a celite pad with excess ethyl acetate. The combined filtrates were concentrated in vacuo and the resulting crude oil was refluxed with conc. aqueous hydrochloric acid (20 mL) for 2.5 h. The resulting reaction mixture was concentrated in vacuo. The crude product was purified by recrystallization in MeOH/EtOAc to give 11-aminoundecanoic acid hydrochloride salt 11 (650 mg, 98%) as a white solid. mp 144-145 °C [lit. 144-145 °C]13; IR (coated on silicon wafer) 3206-2975 (br), 1725, 1584 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 12.0 (br s, 1H), 7.91 (br s, 3H), 2.76-2.73 (m, 2H), 2.19 (t, J = 7.4, 2H), 1.53-1.46 (m, 4H), 1.31-1.22 (m, 12H); ¹³C NMR (100 MHz, DMSO-d₆) δ 174.9, 39.2, 34.2, 29.2, 29.2, 29.0, 27.4, 26.3, 25.0; HRMS (Cl) calcd for C₁₁H₂₀NO₂ [M + Cl]⁻ 202.1807, found 202.1804.

**Methyl 11-Cyanoundec-10-enoate (12a)/Methyl 11-Cyanoundec-9-enoate (12b).** To a solution of aldehyde 4 (1.50 g, 7.49 mmol) and cyanoacetic acid (960 mg, 11.2 mmol) in tetrahydrofuran (15 mL) under nitrogen atmosphere was added DBU (4.56 g, 30.0 mmol). The reaction mixture was heated at 60 °C for 12 h and then was extracted with ethyl acetate (60 mL × 2) and distilled water (60 mL × 2). The combined organic extracts were dried over MgSO₄, filtered, and concentrated in vacuo. Purification by silica gel column chromatography (1:8 v/v, EtOAc:hexane) afforded a mixture of nitriles 12a and 12b (1.44 g, 86%, 12a:12b = 86:14 by GC/MSD) as a colorless liquid: IR (coated on silicon wafer) 2224, 1739, 1583 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.33-7.23 (m, 1H), 6.98 (d, J = 13.4, 1H), 3.67 (s, 3H), 2.31 (t, J = 7.6, 2H), 2.28-2.23 (m, 2H), 1.64-1.59 (m, 2H), 1.53-1.46 (m, 2H), 1.31 (br s, 8H); ¹³C NMR (75 MHz, CDCl₃) δ 142.8, 139.6, 51.5, 34.0, 29.1, 29.0, 29.0, 28.4, 27.7, 24.9; HRMS (Cl) calcd for C₁₁H₁₄NO₂ [M + H]⁺ 244.1549, found 244.1548.

**Methyl 11-Nitroundecanoate (9).** To a solution of nitroolefin 8 (213 mg, 0.88 mmol) in ethyl acetate (2 mL) was added 10 wt % palladium on carbon (10.7 mg, 0.010 mmol). The reaction mixture was stirred at room temperature for 2 h under 3 bar of hydrogen atmosphere and filtered through a celite pad with excess ethyl acetate. The combined filtrates were concentrated in vacuo. Purification by silica gel column chromatography (1:2 v/v, EtOAc:hexane) afforded nitroalkane 9 (210 mg, 98%) as a colorless liquid:
atmosphere and then filtered through a celite pad with excess methanol. The combined organic filtrates were concentrated in vacuo. Purification by silica gel column chromatography (1:4 v/v, EtOAc:hexane) afforded methyl 11-cyano-dodecanoate 13 (2.78 g, 98%) as a colorless liquid: IR (coated on silicon wafer) 2246, 1738 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.69 (3H, s), 1.91-1.85 (m, 2H), 1.51-1.55 (m, 4H), 1.34-1.22 (m, 12H); \(13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 26.8, 25.8, 24.4; HRMS (CI) calcd for C\(_{10}\)H\(_{18}\)NO\(_2\) [M + H\(^+\)]\(^\dagger\) 206.1807, found 206.1807.

Dodecanedioic Acid (14). Methyl 11-cyano-dodecanoate 13 (177 mg, 0.76 mmol) was heated under reflux with conc. aqueous hydrochloric acid (10 mL) for 2.5 h. The resulting mixture was concentrated in vacuo. The residue was purified by recrystallization in water/MeOH to give dodecanedioic acid 14 (175 mg, quantitative) as a white solid. mp 162-163 \(^\circ\)C. IR (KBr) 1744, 1732 cm\(^{-1}\); \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 9.01 (br s, 3H), 2.34 (t, \(J = 7.2\) Hz, 2H), 1.96-1.90 (m, 2H), 1.68-1.60 (m, 4H), 1.46-1.40 (m, 2H), 1.33-1.26 (m, 10H); \(^13\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 174.4, 33.7, 28.9, 28.8, 28.7, 28.6, 24.5; HRMS (CI) calcd for C\(_{12}\)H\(_{22}\)NO\(_2\) [M + H\(^+\)]\(^\dagger\) 231.1596, found 231.1596.

12-Aminododecanoic Acid Hydrochloride Salt (16). To a solution of methyl 11-cyano-dodecanoate 13 (300 mg, 1.29 mmol) in methanol (6 mL) and acetic acid (6 mL) was added 5 wt% Rhodium on carbon (60 mg, 0.029 mmol). The reaction mixture was stirred for 6 h at room temperature under 60 bar of hydrogen atmosphere and then filtered through a celite pad with excess methanol. The combined filtrates were concentrated to afford methyl 12-aminododecanoate acetic acid salt 15 as a white solid. The crude product 15 was used for the next reaction without further purification. mp 79-80 \(^\circ\)C; IR (coated on silicon wafer) 1732 cm\(^{-1}\); \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 6.09 (br s, 3H), 3.66 (s, 2H), 2.77 (t, \(J = 7.6\) Hz, 2H), 2.30 (t, \(J = 7.4\) Hz, 2H), 1.93 (s, 3H), 1.63-1.58 (m, 4H), 1.35-1.23 (m, 14H); \(^13\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 179.0, 174.3, 51.4, 39.6, 34.1, 29.5, 29.5, 29.4, 29.3, 29.2, 29.1, 28.3, 26.7, 25.0, 24.6; HRMS (CI) calcd for C\(_{12}\)H\(_{22}\)NO\(_2\) [M + Na\(^+\)]\(^\dagger\) 230.2120, found 230.2114.

Methyl 12-aminododecanoate acetic acid salt 15 from the above was heated under reflux with conc. aqueous hydrochloric acid (10 mL) for 2.5 h. Concentration in vacuo afforded 12-aminododecanoic acid hydrochloride salt 16 (277 mg, 86%) as a white solid. mp 162 \(^\circ\)C; IR (coated on silicon wafer) 3212-2991 (br), 1726, 1584 cm\(^{-1}\); \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 12.00 (br s, 1H), 8.05 (br s, 3H), 2.77-2.69 (m, 2H), 2.19 (t, \(J = 7.2\) Hz, 2H), 1.56-1.46 (m, 4H), 1.31-1.21 (m, 14H); \(^13\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 174.4, 38.6, 33.6, 28.8, 28.8, 28.7, 28.5, 26.8, 25.8, 24.4; HRMS (CI) calcd for C\(_{12}\)H\(_{22}\)NO\(_2\) [M - Cl\(^-\)]\(^\dagger\) 216.1964, found 216.1960.

Results and Discussion

Herein, we report a divergent process for C\(_{10}\) to C\(_{12}\) polyamide monomers from a common starting material, undecylenic acid 4, which could be produced via pyrolysis of castor oil. Preparation of the C\(_{10}\) monomers from 1 is shown in Scheme 1. Ozonolysis of 1 provided C\(_{10}\) \(\alpha\)-\(\omega\)-dicarboxylic acid 3 via its monoester precursor 2 in quantitative yield after work-up with aq. NaOH. The work-up of the ozonolysis reaction with H\(_2\)O\(_2\) gave the similar results for diacid 3. For the production of C\(_{10}\) \(\omega\)-amino acid, we first prepared the key aldehyde intermediate 4 from ozonolysis of methyl ester of 1. Because aldehyde 4 was labile to autoxidation, it was immediately used after column purification for the next reactions. Catalytic reductive amination of 4 with benzylamine under 40 bar of H\(_2\) gas afforded C\(_{10}\) \(\omega\)-amino ester 5 (Scheme 1).

Initially, we tried the reductive amination of 4 with ammonia, but considerable by-products of dialkylated and trialkylated amines were obtained. A debenzylated intermediate 5\('\) was protected with Boc\(_2\)O to afford 6 in excellent yield. Without the protection, the debenzylation reaction of 5\('\) yielded some unidentified by-products together with the corresponding free amine 5\(\prime\), presumably due to the instability of the free amine when exposed to the air during the isolation. The following simple acidic hydrolysis of 6 gave the desired C\(_{10}\) \(\omega\)-amino acid 7 as its hydrochloride salt. Thus, the C\(_{10}\) \(\omega\)-amino acid monomer 7 was obtained in 79% yield over six steps starting from 1.

For the synthesis of C\(_{11}\) \(\omega\)-amino acid and \(\alpha\)-\(\omega\)-dicarboxylic acid from the C\(_{10}\) key intermediate 4, a nitromethyl group was employed to introduce the desired functional groups as well as one more carbon (Scheme 2). A nitromethyl group is such a versatile functional group that it can be transformed into either an aminomethyl or a carboxyl group. The desired
nitroolefin 8 was produced in excellent yield from 4 in two steps by a sequence of a nitro-aldol reaction (Henry reaction)\(^2\) followed by dehydration with methanesulfonyl chloride (MsCl). The more effective Henry reaction was achieved with excess nitromethane in the presence of stoichiometric amount of NaOH in less than 2 h. A catalytic version of the Henry reaction did not go to completion and use of weaker bases such as KH\(_2\)PO\(_4\), Pr\(_2\)NEt, and piperidine didn’t work at all and most of the starting material was recovered. Although a mixture of four olefinic isomers was obtained, it was not important because they were eventually transformed into the same compound 13 via partial hydrogenation. Selective partial catalytic hydrogenation of 12 (12a and 12b) with Pd/C at low pressure of H\(_2\) (10 bar) gave 13 with the saturated alkyl chain in excellent yield, the key intermediate for both C\(_{12}\) α,ω-dicarboxylic acid and C\(_{12}\) ω-amino acid. The following hydrolysis of 13 under acidic conditions produced the desired C\(_{12}\) α,ω-dicarboxylic acid 14 in quantitative yield.

Further reduction of 13 into 15 was carried out by catalytic hydrogenation with Rh/C at higher pressure (60 bar). The reduction did not proceed at all with other catalysts such as Pt/C or PtO\(_2\) and the starting material was fully recovered. The catalytic reduction with Pd/C or Pd(OH)\(_2\) seemed working but the yield was low and some unknown by-products were observed. The Rh-catalysed reduction was successful in the presence of various acids such as acetic acid, trifluoroacetic acid, and formic acid to give the rather stable product as its ammonium salt. Indeed, we had difficulty in isolating the completely reduced compound as a free amino acid form due to its instability. Among others, the co-solvent system of AcOH and MeOH gave the best yield and purity. Although the complete reduction of 12 into 15 worked well, a stepwise reduction process via 13 was adopted because the direct reduction of 12 was less efficient than the stepwise reduction in terms of the yield and purity. Acidic hydrolysis of 15 then afforded C\(_{12}\) ω-amino acid 16 as its hydrochloride salt. Thus, the C\(_{12}\) α,ω-dicarboxylic acid monomer 14 and the C\(_{12}\) ω-amino acid monomer 16 were obtained in 84% yield over five steps and 72% yield over six steps, respectively, starting from 1.

**Conclusion**

In conclusion, we have developed a versatile and efficient process for three C\(_{10}\) to C\(_{12}\) α,ω-dicarboxylic acid monomers and three C\(_{10}\) to C\(_{12}\) ω-amino acid monomers of polyamides from one common starting material, undecylenic acid 1, which can be easily obtained from castor oil. All of the C\(_{10}\) to C\(_{12}\) monomers were successfully synthesized in good to
excellent yields. The C$_{10}$ α,ω-dicarboxylic acid and ω-amino acid monomers, 3 and 7, were obtained from the ozonolysis of 1 followed by appropriate transformations of the functional groups. The one-carbon extended nitroolefin 8, produced from 1 in four steps and excellent yield, was the common precursor for both C$_{11}$ α,ω-dicarboxylic acid and ω-amino acid monomers, 10 and 11. The two-carbon extended C$_{12}$ α,ω-dicarboxylic acid and ω-amino acid monomers, 14 and 16, were resulted from the common precursor 13 that was produced from 1 in four steps and high yield. It is also noteworthy that most of the reagents and the reaction conditions used in the present study are readily available and adjustable for an industrial development.

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