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A study on the stereochemistry of direct conversion of polyamides to hydroxyesters using monomeric secondary chiral amines as a model compound

Akio Kamimura [a, *], Kosuke Ikeda [a], Yugo Akinari [a], Hiroshi Matsumoto [b], Kouji Kaiso [b]

[a] Department of Applied Chemistry, Yamaguchi University, Ube, 755-8611, Japan
[b] Ube Laboratory, Ube Industries Ltd., Ube, 755-8633, Japan

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ABSTRACT

Stereochemistry of direct conversion of polyamides to hydroxyesters was investigated using model compounds. Optically active secondary-alkyl amines underwent the conversion to corresponding secondary alcohols in moderate yields by treatment with supercritical methanol in the presence of glycolic acid. The reaction progressed through almost completely stereochemical inversion to give secondary alcohols in high yields. Thus, the substitution reaction of the amino group to hydroxyl group progresses through S_N2 type transition state accompanying with stereoinversion.

1. Introduction

Selective method for depolymerization for polymeric material is important for achieving effective chemical recycling of plastics [1]. Recently, we have developed a new strategy to convert polyamides to corresponding monomers [2] as well as monomeric hydroxyester in one-step depolymerization/substitution reaction [3,4]. In the latter reaction, the products, hydroxyesters, were obtained over 70% yield by treatment with supercritical methanol in the presence of glycolic acid. Mechanistic study on the reaction revealed that the reaction progressed through depolymerization reaction to give ω-aminoester followed by substitution reaction of the amino group to the hydroxyl group [5]. Glycolic acid as the additive of the reaction played important role for the substitution reaction, and it is supposed to serve as the nucleophile of the reaction.

From the viewpoint of organic chemistry, substitution of amino group to hydroxyl group is rather rare reactions, and only limited number of the examples taking multistep procedures has been known. For example, such conversion was achieved by through *N*-nitrosamide [6–18]. Other methodologies such as using nitrous acid [19,20], Demijanov rearrangement [21], phase-transfer catalyst [22], and simple alkali salts with high temperature conditions have been known [23]. Benzylic amine is exceptionally reactive towards the substitution reaction [24]. The reason of the difficulty of the conversion is simply owing to poor nucleofugality of the amino group in nucleophilic substitution reactions, and requires assistance to enhance it. In our reaction, the substitution progressed in a high efficiency and we thought that the acidic proton of glycolic acid assisted the substitution reaction by protonation to the amino group. Additionally, our kinetic study indicated that the reaction rate for the substitution step increased in proportion to the amounts of glycolic acid added [5], which reflects that the substitution process is regarded to progress through S_N2 type reaction at the carbon attaching the amino group. To prove the S_N2 mechanism on the process, remaining question is how the stereochemistry of the substrate and product changes during the reaction. If the S_N2 type substitution occurs, high level of stereoinversion at the substituted carbon should be observed. We chose optically active secondary-alkyl amines as model compounds, and exposed the compounds under the same reaction conditions. In this paper, we report that the conversion progressed through almost perfect steric inversion of the substituted carbon, i.e., complete level of the Walden inversion was observed.

* Corresponding author.
E-mail address: ak10@yamaguchi-u.ac.jp (A. Kamimura).

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2. Experimental

2.1. Materials

Optically active secondary alcohols and amines except for 2-aminodecane were purchased from Sigma-Aldrich. (*R*)- and (*S*)-2-aminodecane **1e** were prepared according to the method reported (see below) [25–27].

2.2. Procedures for the conversion of 1-aminooctane to 1-octanol

1-Aminooctane **1a** (100.0 mg, 0.775 mmol), glycolic acid (249.4 mg, 3.28 mmol, 4.2 equivalents), and MeOH (3 g) were added to a 10 mL reaction vessel (stainless steel tube, internal diameter 7.35 mm × 23 cm, capped at both ends by Swagelok nuts) under an argon atmosphere. After sealing, the reaction vessel was placed in a hot oven (270 °C) for the 6 h. The reaction vessel was cooled in a dry-ice/MeOH bath, and the internal standard (1-hexanol) was added. The products were analyzed by GC (Shimadzu GC-2014), Intercap 5 column (internal diameter 0.25 mm × 30 m) and quantified using curve fitting methods. Amounts of the three products, 1-octanol **2a**, 1-octene, **3a**, and 1-methoxyoctane **4a** were quantified to be 73.8 mg (73%), 1.7 mg (2%), and 3.8 mg (3%), respectively.

2.3. Procedures for the conversion of 2-aminooctane to 2-octanol

2-Aminooctane **1b** (100.0 mg, 0.775 mmol), glycolic acid (249.4 mg, 3.28 mmol, 4.2 equivalents), and MeOH (3 g) were added to a 10 mL reaction vessel (stainless steel tube, internal diameter 7.35 mm × 23 cm, capped at both ends by Swagelok nuts) under an argon atmosphere. After sealing, the reaction vessel was placed in a hot oven (270 °C) for the 6 h. The reaction vessel was cooled in a dry-ice/MeOH bath, and the internal standard (1-hexanol) was added. The products were analyzed by GC (Shimadzu GC-2014, Intercap 5 column (internal diameter 0.25 mm × 30 m) and quantified using curve fitting methods. Amounts of the four products, 1-octanol **2a**, 1-octene **3a**, *trans*-2-octene **3b**, and 1-methoxyoctane **4b** were quantified to be 24.8 mg (25%), 34.6 mg (40%), 9.5 mg (11%), and 2.2 mg (2%), respectively.

2.4. Preparation of chiral 2-aminodecane ***1e***

Under nitrogen atmosphere, a solution of 2-decanone (1.4 mL, 7.68 mmol) and (*R*)-(+)-*tert*-butylsulfinamide (798.9 mg, 6.59 mmol) in THF (15 mL) was heated at 60 °C for 18 h in the presence of $Ti(OEt)_4$ (2.7 mL, 12.9 mmol). Then the reaction mixture was cooled to −78 °C. L-selectride (20 mL, 93.6 mmol) was added and the resulting mixture was stirred at the same temperature for 20 h. The reaction was quenched by adding water (10 mL). THF was removed in vacuo and the resulting water phase was extracted with EtOAc (3 × 50 mL). The organic phase was combined, washed with brine (2 × 20 mL) and dried over Na_2SO_4. After filtration, the filtrate was concentrated, and obtained crude product was purified through flash chromatography (silica gel/hexane-EtOAc 3:1 v/v) to give (*S*)-2-aminodecane sulfinamide in 77% yield (1.361 g, 5.07 mmol).

Obtained (*S*)-2-aminodecane sulfinamide (803.3 mg, 3.07 mmol) was dissolved in 4M HCl-dioxiane (20 mL) and methanol (5 mL), and the reaction solution was stirred at room temperature for 24 h. Organic solvent was removed in vacuo and the solid residue was dissolved in water (5 mL), which was washed with ether (5 × 20 mL). Aqueous 3M NaOH (10 mL) was added to the water phase and resulting basified aqueous solution was extracted with ether (5 × 20 mL). The latter organic phase was combined, washed with brine (2 × 20 mL), and dried over Na_2SO_4. After filtration, the filtrate was concentrated, and obtained crude product was purified through flash chromatography (silica gel/hexane-EtOAc 10:1 then 5:1 v/v) to give (*S*)-(+)-2-aminodecane (*S*)-**1e** in 82% yield (397.4 mg, 2.53 mmol).

Yellow oil; $[\alpha]_D$ +5.7 (c 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.85 (m, 1H), 1.48–1.19 (m, 16H), 1.04 (d, J = 6.3 Hz, 3H), 0.86 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 47.1, 40.3, 32.0, 29.8, 29.7, 29.4, 26.5, 24.1, 22.8, 14.2.

(*R*)-(−)-2-aminodecane (*R*)-**1e** was prepared in a similar manner.

Yellow oil; $[\alpha]_D$ −4.9 (c 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.86 (dd, J = 10.9, 5.3 Hz, 1H), 1.36–1.21 (m, 16H), 1.03 (d, J = 6.3 Hz, 3H), 0.87 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 47.0, 40.4, 32.0, 29.8, 29.7, 29.4, 26.5, 24.1, 22.8, 14.2.

2.5. Preparation of chiral secondary alcohols

A solution of (*R*)-(−)-2-aminoheptane **1c** (0.6127 g, 5.32 mmol), glycolic acid (4.2387 g, 55.7 mmol), and MeOH (24 g) were divided into ten portions, and each portion was added to a 10 mL reaction vessel (stainless steel tube, internal diameter 7.35 mm × 23 cm, capped at both ends by Swagelok nuts) under an argon atmosphere. After sealing, the ten reaction vessels were placed in a hot oven (270 °C) for the appropriate time. The reaction vessels were cooled in a dry-ice/MeOH bath, and combined. Crude product was obtained by removal of methanol in vacuo, and obtained (*S*)-(+)-2-heptanol **2c** was isolated by flash chromatography (silica gel/hexane-EtOAc 10:1 then 8:1 v/v). 25% yield (0.1574 g, 1.35 mmol).

Yellow oil; $[\alpha]_D$ +9.6 (c 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.78 (m, J = 6.3 Hz, 1H), 1.50–1.24 (m, 9H), 1.18 (d, J = 6.2 Hz, 3H), 0.88 (t, J = 6.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 68.3, 39.4, 31.9, 25.5, 23.6, 22.7, 14.1.

Other chiral alcohols **2** were obtained in a similar manner.

(*R*)-(−)-2-heptanol **2c**: Yellow oil; $[\alpha]_D$ −8.9° (c 1.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.86–3.70 (m, 1H), 1.50–1.24 (m, 9H), 1.18 (d, J = 6.2 Hz, 3H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 68.3, 39.4, 31.9, 25.5, 23.6, 22.7, 14.1.

(*S*)-(+)-2-octanol **2b**: Yellow oil; $[\alpha]_D$ +7.3 (c 1.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.77 (m, J = 7.3 Hz, 1H), 1.47–1.24 (m, 11H), 1.17 (dd, J = 6.1, 1.0 Hz, 3H), 0.87 (t, J = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 68.3, 39.5, 31.9, 29.4, 25.8, 23.5, 22.7, 14.2.

(*R*)-(−)-2-octanol **2b**: Yellow oil; $[\alpha]_D$ −5.8 (c 1.15, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.77 (m, J = 6.2 Hz, 1H), 1.47–1.24 (m, 11H), 1.16 (dd, J = 6.1, 1.3 Hz, 3H), 0.86 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 68.2, 39.4, 31.9, 29.4, 25.8, 23.5, 22.7, 14.1.

(*S*)-(+)-2-nonanol **2d**: Yellow oil; $[\alpha]_D$ +8.0 (c 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.78 (m, J = 6.2 Hz, 1H), 1.46–1.25 (m, 13H), 1.18 (dd, J = 6.1, 1.9 Hz, 3H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 68.3, 39.5, 31.9, 29.7, 29.4, 25.9, 23.6, 22.7, 14.2.

(*R*)-(−)-2-nonanol **2d**: Yellow oil; $[\alpha]_D$ −8.0 (c 1.00, $CHCl_3$); ^{1}H NMR($CDCl_3$, 500 MHz) δ 3.78 (m, J = 7.4 Hz, 1H), 1.59 (d, J = 1.6 Hz, 1H), 1.46–1.25 (m, 12H), 1.17 (dd, J = 6.2, 2.5 Hz, 3H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 68.3, 39.5, 31.9, 29.7, 29.4, 25.9, 23.6, 22.7, 14.2.

(*S*)-(+)-2-decanol **2e**: Yellow oil; $[\alpha]_D$ +8.4 (c 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.78 (m, J = 7.2 Hz, 1H), 1.50–1.23 (m, 15H), 1.18 (d, J = 6.2 Hz, 3H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 68.3, 39.5, 32.0, 29.7, 29.7, 29.4, 25.9, 23.6, 22.8, 14.2.

(*R*)-(−)-2-decanol **2e**: Yellow oil; $[\alpha]_D$ −9.3 (c 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.78 (m, J = 7.0 Hz, 1H), 1.50–1.23 (m, 15H), 1.18 (d, J = 6.2 Hz, 3H), 0.87 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 68.3, 39.5, 32.0, 29.7, 29.7, 29.4, 25.9, 23.6, 22.8, 14.2.

2.6. Benzoylation of chiral 2-alkanols

(*S*)-(+)-2-heptanol **2c** (0.1347 g, 1.16 mmol) was added to a solution of benzoyl anhydride (0.4693 g, 2.07 mmol), Et_3N (0.3 mL) and DMAP (0.0765 g, 0.063 mmol) in CH_2Cl_2 (2 mL), and the reaction mixture was stirred at room temperature for 17 h. Aqueous NH_4Cl (5 mL) was added and the resulting mixture was extracted with CH_2Cl_2 (3 × 20 mL). Combined organic phase was washed with brine (2 × 30 mL) and dried over Na_2SO_4. After filtration, the filtrate was concentrated and the residue was subjected to flash chromatography (silica gel/hexane-EtOAc 8:1 then 5:1 v/v) to give (*S*)-(+)-2-benzoyloxyheptane **9c** in 96% yield (0.2439 g, 1.11 mmol).

Yellow oil; $[\alpha]_D$ +34.1 (c 1.02, $CHCl_3$); chiral HPLC analysis with DAICEL CHIRALCEL OB-H (4.6 mm i.d. × 25 cm) eluted by hexane 0.5 mL/min at 25 °C. t_R 12.2 min (minor), t_R 13.1 min (major), 98%ee; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.04 (d, *J* = 7.3 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 6.8 Hz, 2H), 5.15 (m, *J* = 6.0 Hz, 1H), 1.77–1.24 (m, 8H), 1.33 (dd, *J* = 6.3, 2.1 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.3, 132.8, 131.0, 129.6, 128.4, 71.8, 36.1, 31.8, 25.2, 22.6, 20.2, 14.1.

Other chiral benzoate **9** were obtained in a similar manner.

(*R*)-(−)-2-benzoyloxyheptane **9c**: Yellow oil; $[\alpha]_D$ −30.5 (c 1.01, $CHCl_3$); chiral HPLC analysis with DAICEL CHIRALCEL OB-H (4.6 mm i.d. × 25 cm) eluted by hexane 0.5 mL/min at 25 °C. t_R 12.2 min (major), t_R 13.2 min (minor), 97%ee; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.04 (d, *J* = 6.7 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 2H), 5.15 (m, *J* = 6.3 Hz, 1H), 1.77–1.24 (m, 8H), 1.33 (dd, *J* = 6.3, 1.7 Hz, 3H), 0.87 (t, *J* = 6.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.3, 132.8, 131.0, 129.6, 128.4, 71.8, 36.1, 31.8, 25.2, 22.6, 20.2, 14.1.

(*S*)-(+)-2-benzoyloxyoctane **9b**: Yellow oil; $[\alpha]_D$ +34.7 (c 1.04, $CHCl_3$); chiral HPLC analysis with DAICEL CHIRALCEL OB-H (4.6 mm i.d. × 25 cm) eluted by hexane 0.5 mL/min at 25 °C. t_R 11.2 min (minor), t_R 12.2 min (major), 97%ee; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.04 (d, *J* = 8.1 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 8.5 Hz, 2H), 5.15 (m, *J* = 6.0 Hz, 1H), 1.81–1.24 (m, 10H), 1.33 (d, *J* = 6.2 Hz, 3H), 0.87 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR($CDCl_3$, 125 MHz) δ 166.3, 132.8, 131.0, 129.6, 128.4, 71.8, 36.2, 31.8, 29.3, 25.5, 22.7, 20.2, 14.1.

(*R*)-(−)-2-benzoyloxyoctane **9b**: Yellow oil; $[\alpha]_D$ −31.0 (c 1.01, $CHCl_3$); chiral HPLC analysis with DAICEL CHIRALCEL OB-H (4.6 mm i.d. × 25 cm) eluted by hexane 0.5 mL/min at 25 °C. t_R 11.1 min (major), t_R 12.2 min (minor), 98%ee; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.04 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 5.15 (m, *J* = 5.9 Hz, 1H), 1.81–1.24 (m, 10H), 1.33 (d, *J* = 6.3 Hz, 3H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR($CDCl_3$, 125 MHz) δ 166.3, 132.8, 131.0, 129.6, 128.4, 71.8, 36.2, 31.8, 29.3, 25.5, 22.7, 20.2, 14.2.

(*S*)-(+)-2-benzoyloxynonane **9d**: Yellow oil; $[\alpha]_D$ +29.5 (c 1.00, $CHCl_3$); chiral HPLC analysis with DAICEL CHIRALCEL OB-H (4.6 mm i.d. × 25 cm) eluted by hexane 0.5 mL/min at 25 °C. t_R 10.4 min (minor), t_R 11.8 min (major), 98%ee; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.04 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 5.15 (m, *J* = 6.0 Hz, 1H), 1.78–1.22 (m, 12H), 1.33 (dd, *J* = 6.2, 1.4 Hz, 3H), 0.86 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.3, 132.8, 131.0, 129.6, 128.4, 71.8, 36.1, 31.9, 29.5, 29.3, 25.5, 22.7, 20.2, 14.2.

(*R*)-(−)-2-benzoyloxynonane **9d**: Yellow oil; $[\alpha]_D$ −30.1 (c 1.00, $CHCl_3$); chiral HPLC analysis with DAICEL CHIRALCEL OB-H (4.6 mm i.d. × 25 cm) eluted by hexane 0.5 mL/min at 25 °C. t_R 10.6 min (major), t_R 12.0 min (minor), 97%ee; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.04 (d, *J* = 7.8 Hz, 2H), 7.54 (t, *J* = 7.1 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 5.14 (m, *J* = 5.8 Hz, 1H), 1.77–1.22 (m, 12H), 1.33 (d, *J* = 6.2 Hz, 3H), 0.86 (t, *J* = 6.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.3, 132.8, 131.0, 129.6, 128.4, 71.8, 36.1, 31.9, 29.5, 29.3, 25.5, 22.7, 20.2, 14.2.

(*S*)-(+)-2-benzoyloxydecane **9e**: Yellow oil; $[\alpha]_D$ +29.2 (c 0.99, $CHCl_3$); chiral HPLC analysis with DAICEL CHIRALCEL OB-H (4.6 mm i.d. × 25 cm) eluted by hexane 0.5 mL/min at 25 °C. t_R 10.2 min (minor), t_R 12.0 min (major), 95%ee; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.04 (d, *J* = 8.2 Hz, 2H), 7.53 (t, *J* = 6.8 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 5.14 (m, *J* = 6.0 Hz, 1H), 1.79–1.22 (m, 14H), 1.33 (d, *J* = 6.4 Hz, 3H), 0.86 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.3, 132.8, 131.0, 129.6, 128.4, 71.8, 36.1, 31.9, 29.6 (2C), 29.3, 25.5, 22.8, 20.2, 14.2.

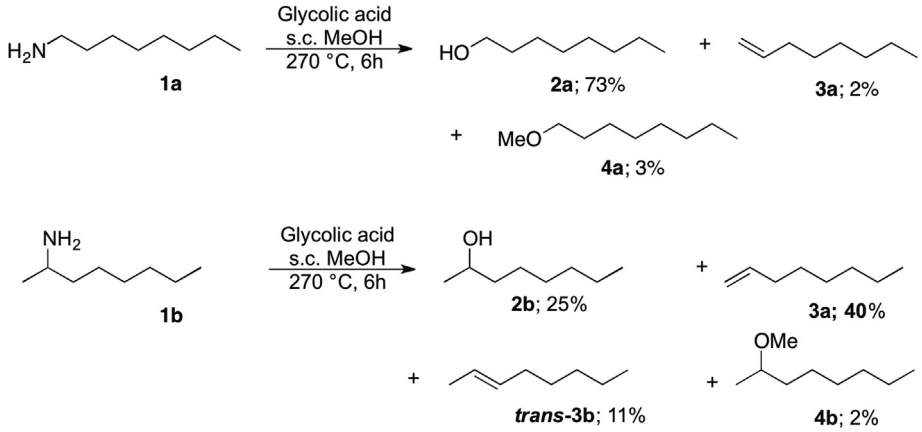
(*R*)-(−)-2-benzoyloxydecane **9e**: Yellow oil; $[\alpha]_D$ −28.4 (c 1.00, $CHCl_3$); chiral HPLC analysis with DAICEL CHIRALCEL OB-H (4.6 mm i.d. × 25 cm) eluted by hexane 0.5 mL/min at 25 °C. t_R 10.2 min (major), t_R 12.1 min (minor), 94%ee; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 2H), 5.14 (m, *J* = 5.9 Hz, 1H), 1.78–1.22 (m, 14H), 1.33 (d, *J* = 6.3 Hz, 3H), 0.86 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.3, 132.8, 131.0, 129.6, 128.4, 71.9, 36.1, 31.9, 29.6 (2C), 29.3, 25.5, 22.8, 20.2, 14.2.

3. Results and discussion

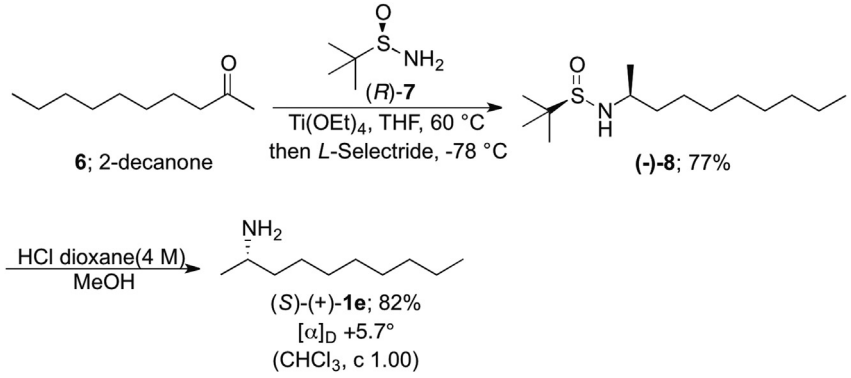
We firstly examined the substitution reaction of primary-alkyl and secondary-alkyl amines. We employed 1-aminooctane **1a** and 2-aminooctane **1b** as the model compounds, and exposed them to supercritical methanol in the presence of glycolic acid, which is exactly the same conditions of we employed for the treatment of polyamides. Compounds **1** were smoothly consumed in the both reactions and products were identified and quantified by GC-MS analyses (Scheme 1). For example, 1-aminooctane **1a** afforded 1-octanol **2a** as the major product in 73% yield. We also detected the formation of small amounts of 1-octene **3a** in 2% and 1-methoxyoctane **4a** in 3%. These results are consistent with the results obtained from the actual depolymerization reaction, in which primary alcohol was mainly generated over 70% yields along with small amounts of alkenes [5]. Thus, use of simple aliphatic amines as a model compound is effective to probe the reaction mechanism of the depolymerization reaction of polyamides.

The product distribution in the reaction of secondary-alkyl amine was, however, different from above results. Treatment of 2-aminooctane **1b** under the same reaction conditions resulted in the smooth consumption of **1b** and similar products were detected by GC analyses that provided identification and quantification of the products. In this reaction 2-octanol **2b** became a minor product and was obtained in 25% yield. The major of the products were two types of alkenes, which were 1-octene (**3a**) in 40% yield, *trans*-2-octene (*trans*-**3b**) in 11%. Formation of small amounts of 2-methoxyoctane (**4b**) was also observed. Thus, products of the reaction were basically the same as the reaction of 1-octanol **1a**, but the product ratio changed very much; the elimination reaction occurred as a main process of the reaction of a secondary-alkyl amine. These results suggests that the sterically hindered the secondary carbon suppresses the reaction rate for the substitution and the elimination process is preferred as the alternative process. Note that 1-alkene **3a** was formed much more than the formation of 2-alkene **3b**. This is probably because the dimethylamino group in the intermediate, which was not a good leaving group even when it was protonated, preferred the Hoffmann elimination process (see below).

We then examined optically active secondary-alkyl amines for the reaction to see how the stereochemistry changed during the substitution reaction. Optically active 2-aminoheptane **1c**, 2-amininononane **1d**, and 2-aminooctane **1b** were commercially available, while 2-aminodecane **1e** was not. Thus, we prepared them via reported method [27]. Outline of the preparation is illustrated in Scheme 2.



Scheme 1. Conversion of primary and secondary amines under the depolymerization conditions.



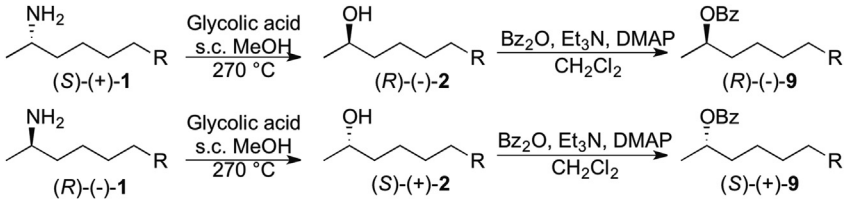
Scheme 2. Preparation of optically active 2-decylamine.

Commercially available chiral sulfinamine (*R*)-**7** was treated with 2-dodecanone **6** in the presence of $Ti(OEt)_4$ and corresponding sulfinimine was obtained. This intermediate underwent stereoselective reduction by L-Selectride to give (−)-**8** in 77% yield. Compound **8** consisted with almost single isomer, which indicates the reduction progressed in a highly stereoselective manner. Removal of the *N*-sulfinyl group was readily achieved by treatment with acidic dioxane solution and we succeeded to prepare (*S*)-(+)-**1e** in 82% yield. The antipode, (*R*)-(−)-**1e,** was prepared in a similar manner.

Both enantiomers of each amine were examined for the substitution reaction with supercritical methanol in the presence of glycolic acid. The results are summarized in Scheme 3.

We needed to determine the optical rotation of the product alcohols, and isolated alcohol products **2b** to **2e**. For example, (*R*)-(−)-2-aminoheptane **1c** gave 2-heptanol **2c** in 25% isolated yield (entry 2). The optical rotation of the obtained alcohol **2c** was measured to be +9.6, which suggested that the absolute configuration of **2c** is *S* [28]. Other products **2** from optically active amine **1** also gave a similar result, and the sign of the optical rotation was always opposite between the products and starting amines. However, it was very difficult to determine enantiomeric excesses of products **2** by chiral HPLC techniques, we converted alcohol **2** to benzoate **9b** to **9e**. The esterification progressed smoothly by treatment with benzoyl anhydride in the presence of DMAP (*N,N*-dimethylaminopyridine) and desired benzoates **9** were obtained in good yields. For example, (+)-**2c** gave benzoate **9c** in 96% yield (entry 3). Benzoates **9** were readily detected by HPLC analyses as well as gave good separation between the both enantiomers using CHRAL-CEL OB-H. HPLC analyses for all products indicated that all of benzoate **9** contained high enantiomeric excess. The observation clearly suggested that the substitution reaction progressed in a stereospecific manner, and almost complete level of stereoinversion occurred during the substitution reaction. As we previously reported [5], kinetic study suggested that the substitution process in the depolymerization reaction was a second-order reaction because the reaction rate increased in proportion to the concentration of glycolic acid added. The present model study showed that the substitution reaction of amines accompanies with almost complete level of stereoinversion at the substituted carbon. Thus, the present substitution reaction of amines to alcohols progressed through S_N2 reaction mechanism.

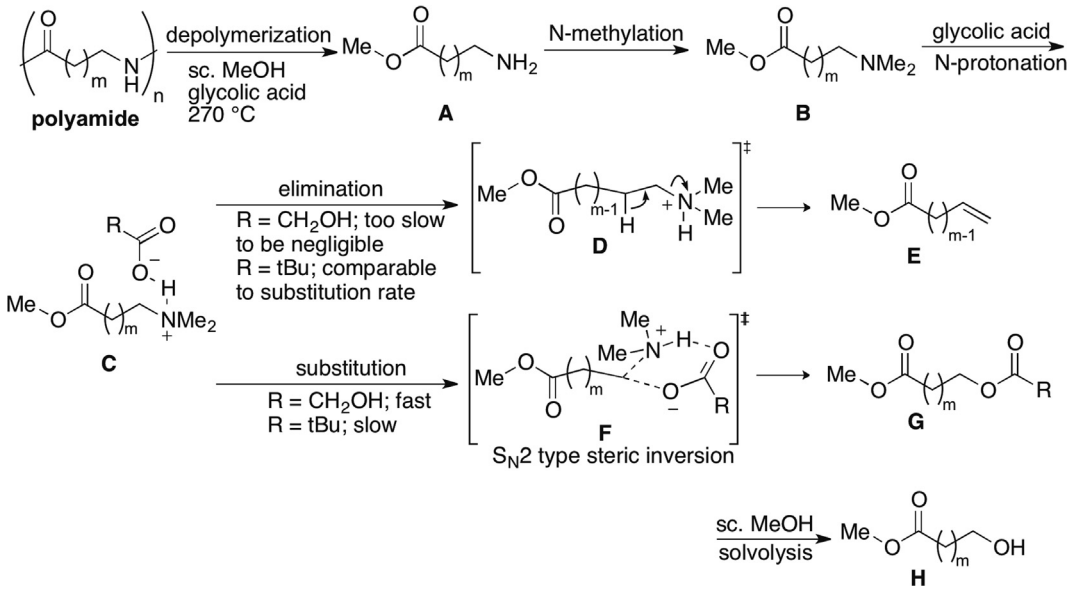
Combining all of the results, we propose mechanism of the substitution process of amines to alcohols as illustrated in Scheme 4. Polyamides firstly undergo depolymerization to give monomeric aminoesters **A**, which are *N*-methylated by the presence of supercritical methanol, giving tertiary amine intermediates **B**, because supercritical methanol is known to work as a methylation agent [29–31]. Then glycolic acid protonates to the tertiary amine to form ammonium cation **C**. This protonation should be necessary to make the amine unit be a good leaving group. The oxygen atom of glycolate anion attacks the carbon from the rear side of the ammonium cation to give glycolate intermediate **G**, which then readily converted to alcohol **H** through transesterification reaction with methanol. During the process, the six-membered ring transition state **F** is highly likely. When pivalic acid is used, the rate for S_N2 process decreases because of the steric hindrance of pivalate anion as the nucleophile, and elimination process becomes competitive



entry	1	R	2; Yield (%)[a]	$[\alpha]_D$	9; Yield (%)[a]	$[\alpha]_D$	ee%[b]
1	(*S*)-(+)-**1c**	CH_3	(*R*)-**2c**; 17%	-8.9	84%	-30.5	97
2	(*R*)-(-)-**1c**	CH_3	(*S*)-**2c**; 25%	+9.6	96%	+34.1	98
3	(*S*)-(+)-**1b**	C_2H_5	(*R*)-**2b**; 13%	-5.8	89%	-31.0	98
4	(*R*)-(-)-**1b**	C_2H_5	(*S*)-**2b**; 17%	+7.3	40%	+34.7	97
5	(*S*)-(+)-**1d**	C_3H_7	(*R*)-**2d**; 24%	-8.0	76%	-30.1	97
6	(*R*)-(-)-**1d**	C_3H_7	(*S*)-**2d**; 32%	+8.0	72%	+29.5	98
7	(*S*)-(+)-**1e**	C_4H_9	(*R*)-**2e**; 30%	-9.3	78%	-28.4	94
8	(*R*)-(-)-**1e**	C_4H_9	(*S*)-**2e**; 27%	+8.4	85%	+29.2	95

a : isolated yield
b : from CHIRALCEL OB-H

Scheme 3. Conversion of optically active secondary amines by treatment with supercritical methanol in the presence of glycolic acid.



Scheme 4. The reaction mechanism of the depolymerization/conversion of polyamides under supercritical methanolic conditions.

and alkene **E** is formed. Indeed, the yield of alkene **E** increased to 41% when polyamide 12 was treated with supercritical methanol in the presence of 8 equivalents of pivalic acid [4].

4. Conclusions

In conclusion, we clarified the stereochemical course of the substitution reaction of monomer products of polyamides to give corresponding alcohols. As a chemical feedstock, the substituted products are generally more highly valuable than simple monomer of polyamides. This basic investigation will give good information on the reaction mechanism, which will be useful for further improvement of the reaction for plastic chemical recycling.

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