

Facile Syntheses of Aromatic Polyesters Bearing Alicyclic Units in the Main Chains

By Katsuya MAEYAMA,* Keita AKIBA, and Hiromu SAITO

Interfacial polycondensation of cyclohexanedicarbonyl dichlorides and adamantanedicarbonyl dichloride with bisphenols in 2 M NaOH aq./CHCl₃ afforded semi-aromatic polyesters. Glass transition temperatures (T_g 's) of the resulting polyesters are in the range of 110–222 °C. Temperatures where 5% weight losses of the polyesters occur in N₂ are in the range of 304–448 °C. Polyesters **4** and **10**, which include *trans*-1,2-cyclohexanediyl and 1,3-adamantanedicarbonyl units, respectively, have excellent solubility in organic solvents. The polyester films **10a,b,e**, which are prepared by casting from CHCl₃, have excellent transparency.

KEY WORDS: Polyesters / Alicyclic Dicarboxyl Units / Excellent Solubility / Excellent Transparency /

Recently, high-performance materials with excellent thermal stability and transparency have been much attracted with the rapid advance of optic and electronic technology.¹ Although PMMA and PC have remarkable transparency, their glass transition temperatures are relatively low. Development of high-performance materials with more excellent thermal stability and transparency has been indispensable.²

Wholly aromatic polyesters have excellent thermal stability and impact strength.^{3–6} The wholly aromatic polyester derived from bisphenol A and terephthalic acid is a crystalline polymer. On the other hand, U polymer[®], which is derived from bisphenol A and *m,p*-mixed phthalic acids, has excellent thermal stability and transparency.⁴ These facts suggest that disorder of molecular sequence by copolymerization is one approach to obtain transparent and thermally stable materials.

Another approach is introduction of alicyclic units to polymer skeletons. Polyimides,^{7–9} poly(benzoxazole)s,¹⁰ and polyolefins^{11,12} containing alicyclic units derived from norbornene and adamantane derivatives have been recently reported and partly applied to lithographic technique.¹⁰ Introduction of alicyclic units to aromatic polymer skeletons increases transparency with small decrease of thermal stability. This motivated us to synthesize alicyclic unit-containing aromatic polyesters with excellent thermal stability and transparency.

In this paper, we would like to report the syntheses of aromatic polyesters containing alicyclic dicarbonyl units through interfacial polycondensation of alicyclic dicarbonyl dichlorides with several aromatic diols, in particular, bisphenols. Thermal and optical properties of the resulting polyesters are also described.

EXPERIMENTAL

Materials

Cyclohexanedicarboxylic acids **1** and **5**, aromatic diols **3a,e**

h, PCl₅, and Bu₄NBr were purchased from Tokyo Kasei Kogyo Co. Aromatic diols **3b-d** were purchased from Wako Pure Chemical Industries. SOCl₂ was purchased from Kanto Chemical Co. These reagents and CHCl₃ were used without any purification. Cyclohexanedicarbonyl dichlorides **2** and **6** were prepared through the reactions of dicarboxylic acids **1** and **5** with PCl₅ at room temperature, respectively. 1,3-Adamantanedicarbonyl dichloride (**9**) was prepared through the reaction of dicarboxylic acid **8** with SOCl₂.

Instruments

¹H NMR spectra were recorded on a JEOL JNM-AL-300 (300 MHz). Chemical shifts were expressed in ppm relative to internal standard of Me₄Si (δ , 0.00). ¹³C NMR spectra were recorded on a JEOL JNM-AL-300 (75 MHz) and a JEOL JNM-ECX-400 (100 MHz). Chemical shifts were expressed in ppm relative to internal standard of CDCl₃ (δ , 77.0). IR measurement was recorded on a JEOL FT/IR-4100. Gel permeation chromatography (GPC) measurements were carried out at a flow rate of 1.0 mL min⁻¹ at 40 °C using CHCl₃ as an eluent on a Shimadzu SPD-6A equipped with a UV detector (300 nm) and a Shodex KD-806M column. Glass transition temperatures (T_g) were determined on the basis of DSC curves. DSC curves were recorded on a Rigaku DSC-8230 differential scanning calorimeter with a heating rate of 10 K min⁻¹. Thermal degradation temperatures (T_{d5}) were determined on the basis of a TGA thermogram. The TGA thermogram was recorded on a Rigaku TG-8120 thermogravimeter with a heating rate of 10 K min⁻¹. UV-vis spectra were recorded on a JEOL V-630 spectrophotometer.

General Procedure for Synthesis of Polyesters **4**, **7**, and **10**

To a dried 30 mL one-necked flask were added diol **3** (0.5 mmol), tetrabutylammonium bromide (8.0 mg, 0.025 mmol), and aqueous 2 M NaOH (0.5–1.5 mL). After a CHCl₃

Department of Organic and Polymer Materials Chemistry, Graduate School of Technology, Tokyo University of Agriculture and Technology, Koganei 184-8588, Japan

*To whom correspondence should be addressed (Tel: +81-42-388-7475, Fax: +81-42-388-7291, E-mail: maeyama@cc.tuat.ac.jp).

solution (1 mL) of alicyclic dicarbonyl dichloride **2**, **6**, or **9** (0.5 mmol) was added, the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was neutralized with aqueous 2 M HCl and quenched by pouring it into methanol in a beaker. The solid was collected with suction filter and washed with water and methanol three times. The collected solid was dried *in vacuo* at 30 °C to obtain the corresponding polyester.

Polyester 4a: $^1\text{H NMR } \delta$ (300 MHz, CDCl_3): 1.37–1.68 (4H, m), 1.76–2.02 (2H, m), 2.25–2.39 (2H, m), 2.80–3.00 (2H, m), 6.93–7.01 (8H, m) ppm. $^{13}\text{C NMR } \delta$ (75 MHz, CDCl_3): 25.1, 28.8, 44.8, 119.5, 122.6, 146.1, 154.6, 173.6 ppm. IR ν (neat): 1753 cm^{-1} . Anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_5$: C 70.99%, H 5.36%. Found, C 70.12%, H 5.11%.

Polyester 4b: $^1\text{H NMR } \delta$ (300 MHz, CDCl_3): 1.39–1.75 (4H, m), 1.87–2.02 (2H, m), 2.33–2.45 (2H, m), 2.92–3.07 (2H, m), 7.18 (4H, d, $J = 8.7$ Hz), 7.82 (4H, d, $J = 8.7$ Hz) ppm. $^{13}\text{C NMR } \delta$ (75 MHz, CDCl_3): 25.0, 28.7, 44.8, 121.5, 131.5, 134.9, 153.9, 172.9, 194.2 ppm. IR ν (neat): 1658, 1753 cm^{-1} . Anal. Calcd. for $\text{C}_{21}\text{H}_{18}\text{O}_5$: C 71.99% H 5.18%. Found, C 70.01% H 4.90%.

Polyester 4c: $^1\text{H NMR } \delta$ (300 MHz, CDCl_3): 1.36–1.45 (2H, m), 1.51–1.65 (2H, m), 1.63 (6H, s), 1.85–1.97 (2H, m), 2.23–2.38 (2H, m), 2.87–3.00 (2H, m), 6.94 (4H, d, $J = 8.7$ Hz), 7.18 (4H, d, $J = 8.7$ Hz) ppm. $^{13}\text{C NMR } \delta$ (75 MHz, CDCl_3): 25.1, 28.8, 30.9, 42.4, 44.8, 120.8, 127.8, 147.8, 148.5, 173.5 ppm. IR ν (neat): 1752 cm^{-1} . Anal. Calcd. for $\text{C}_{23}\text{H}_{24}\text{O}_4$: C 75.80%, H 6.64%. Found, C 74.20%, H 6.51%.

Polyester 4d: $^1\text{H NMR } \delta$ (300 MHz, CDCl_3): 1.33–1.67 (4H, m), 1.82–1.99 (2H, m), 2.25–2.41 (2H, m), 2.87–3.04 (2H, m), 7.09 (4H, d, $J = 9.0$ Hz), 7.37 (4H, d, $J = 9.0$ Hz) ppm. $^{13}\text{C NMR } \delta$ (75 MHz, CDCl_3): 25.1, 28.7, 44.8, 63.9 (sept, $^2\text{J}_{\text{CF}}$, $J = 26$ Hz), 121.2, 124.0 (q, $^1\text{J}_{\text{CF}}$, $J = 279$ Hz), 130.6, 132.2, 151.0, 173.1 ppm. IR ν (neat): 1759 cm^{-1} . Anal. Calcd. for $\text{C}_{23}\text{H}_{18}\text{F}_6\text{O}_4$: C 58.48%, H 3.84%. Found, C 58.29%, H 4.03%.

Polyester 4e: $^1\text{H NMR } \delta$ (300 MHz, CDCl_3): 1.35–1.69 (10H, m), 1.86–1.92 (2H, m), 2.15–2.34 (6H, m), 2.89–2.94 (2H, m), 6.94 (4H, d, $J = 8.7$ Hz), 7.21 (4H, d, $J = 8.7$ Hz) ppm. $^{13}\text{C NMR } \delta$ (75 MHz, CDCl_3): 22.7, 25.1, 26.2, 28.8, 37.3, 44.8, 45.7, 121.0, 128.2, 145.7, 148.3, 173.4 ppm. IR ν (KBr): 1752 cm^{-1} . Anal. Calcd. for $\text{C}_{26}\text{H}_{28}\text{O}_4$: C 77.20%, H 6.98%. Found, C 76.46%, H 6.52%.

Polyester 4f: $^1\text{H NMR } \delta$ (300 MHz, CDCl_3): 0.97–1.11 (2H, m), 1.43–1.66 (6H, m), 2.42–2.61 (2H, m), 7.02–7.08 (2H, m), 7.14–7.24 (4H, m), 7.27–7.35 (2H, m) ppm. $^{13}\text{C NMR } \delta$ (75 MHz, CDCl_3): 24.9, 27.6, 44.2, 122.4, 125.6, 128.9, 130.2, 131.1, 148.2, 173.1 ppm. IR ν (neat): 1753 cm^{-1} . Anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_4$: C 74.52%, H 5.63%. Found, C 73.80%, H 5.61%.

Polyester 4g: $^1\text{H NMR } \delta$ (300 MHz, CDCl_3): 1.34–1.66 (4H, m), 1.82–1.96 (2H, m), 2.25–2.37 (2H, m), 2.85–2.95 (2H, m), 7.03 (8H, brs) ppm. $^{13}\text{C NMR } \delta$ (75 MHz, CDCl_3): 25.1, 28.7, 44.8, 122.3, 148.0, 173.3 ppm. IR ν (neat): 1754 cm^{-1} . Anal. Calcd. for $\text{C}_{14}\text{H}_{14}\text{O}_4$: C 68.28%, H 5.73%. Found, C 67.85%, H 5.86%.

Polyester 4h: $^1\text{H NMR } \delta$ (300 MHz, CDCl_3): 1.32–1.66 (4H, m), 1.81–2.00 (2H, m), 2.21–2.36 (2H, m), 2.80–2.96 (2H, m), 6.82 (1H, brs), 6.93 (2H, d, $J = 8.7$ Hz), 7.30 (1H, t, $J = 8.7$ Hz) ppm. $^{13}\text{C NMR } \delta$ (75 MHz, CDCl_3): 25.1, 28.7, 44.8, 115.2, 119.1, 129.7, 151.1, 173.0 ppm. IR ν (neat): 1756 cm^{-1} . Anal. Calcd. for $\text{C}_{14}\text{H}_{14}\text{O}_4$: C 68.28%, H 5.73%. Found, C 67.77%, H 5.61%.

Polyester 7a: $^1\text{H NMR } \delta$ (300 MHz, CDCl_3): 1.65–1.73 (4H, m), 2.27–2.35 (4H, m), 2.5–3–1–2.65 (2H, m), 6.98–7.07 (8H, m) ppm. IR ν (neat): 1751 cm^{-1} . Anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_5$: C 70.99%, H 5.36%. Found, C 69.20%, H 5.16%.

Polyester 7b: Insoluble to CHCl_3 . IR ν (neat): 1654, 1754 cm^{-1} . Anal. Calcd. for $\text{C}_{21}\text{H}_{18}\text{O}_5$: C 71.99% H 5.18%. Found, C 71.34%, H 5.11%.

Polyester 7c: $^1\text{H NMR } \delta$ (300 MHz, CDCl_3): 1.51–1.65 (4H, m), 1.67 (6H, s), 2.19–2.35 (4H, m), 2.52–2.65 (2H, m), 6.97 (4H, d, $J = 8.7$ Hz), 7.22 (4H, d, $J = 8.7$ Hz) ppm. $^{13}\text{C NMR } \delta$ (75 MHz, CDCl_3): 27.9, 30.9, 42.4, 51.6, 120.8, 127.4, 147.8, 148.5, 173.9 ppm. IR ν (neat): 1753 cm^{-1} . Anal. Calcd. for $\text{C}_{23}\text{H}_{24}\text{O}_4$: C 75.80%, H 6.64%. Found, C 75.10%, H 6.51%.

Polyester 7d: $^1\text{H NMR } \delta$ (300 MHz, CDCl_3): 1.61–1.77 (4H, m), 2.21–2.37 (4H, m), 2.55–2.69 (2H, m), 7.12 (4H, d, $J = 8.7$ Hz), 7.42 (4H, d, $J = 8.7$ Hz) ppm. $^{13}\text{C NMR } \delta$ (75 MHz, CDCl_3): 27.7, 42.3, 63.9 (sept, $^2\text{J}_{\text{CF}}$, $J = 26$ Hz), 121.4, 123.9 (q, $^1\text{J}_{\text{CF}}$, $J = 283$ Hz), 130.5, 131.4, 151.1, 173.3 ppm. IR ν (neat): 1759 cm^{-1} . Anal. Calcd. for $\text{C}_{23}\text{H}_{18}\text{F}_6\text{O}_4$: C 58.48%, H 3.84%. Found, C 58.16%, H 3.57%.

Polyester 7e: $^1\text{H NMR } \delta$ (300 MHz, CDCl_3): 1.35–1.82 (10H, m), 2.12–2.35 (8H, m), 2.45–2.66 (2H, m), 6.91–7.02 (2H, m), 7.18–7.30 (2H, m) ppm. $^{13}\text{C NMR } \delta$ (75 MHz, CDCl_3): 22.7, 26.2, 27.9, 37.3, 42.4, 45.7, 121.0, 128.2, 145.8, 148.3, 173.9 ppm. IR ν (KBr): 1751 cm^{-1} . Anal. Calcd. for $\text{C}_{26}\text{H}_{28}\text{O}_4$: C 77.20%, H 6.98%. Found, C 77.34%, H 6.72%.

Polyester 10a: $^1\text{H NMR } \delta$ (300 MHz, CDCl_3): 1.75–1.85 (2H, m), 2.01–2.12 (8H, m), 2.25–2.33 (2H, m), 2.33–2.40 (2H, m), 6.97–7.06 (8H, m) ppm. $^{13}\text{C NMR } \delta$ (75 MHz, CDCl_3): 27.6, 35.1, 37.8, 39.4, 41.2, 119.4, 122.6, 146.3, 154.6, 175.2 ppm. IR ν (neat): 1748 cm^{-1} . Anal. Calcd. for $\text{C}_{24}\text{H}_{22}\text{O}_5$: C 73.83%, H 5.68%. Found, C 72.99%, H 5.48%.

Polyester 10b: $^1\text{H NMR } \delta$ (300 MHz, CDCl_3): 1.75–1.93 (2H, m), 2.02–2.22 (8H, m), 2.29–2.37 (2H, m), 2.37–2.45 (2H, m), 7.21 (4H, d, $J = 8.4$ Hz), 7.86 (4H, d, $J = 8.4$ Hz) ppm. $^{13}\text{C NMR } \delta$ (75 MHz, CDCl_3): 27.6, 35.1, 37.7, 39.3, 41.4, 121.5, 131.5, 134.8, 154.1, 174.6, 194.3 ppm. IR ν (neat): 1661, 1750 cm^{-1} . Anal. Calcd. for $\text{C}_{25}\text{H}_{22}\text{O}_5$: C 74.61%, H 5.51%. Found, C 73.33%, H 5.47%.

Polyester 10c: $^1\text{H NMR } \delta$ (300 MHz, CDCl_3): 1.65 (6H, brs), 1.76–1.82 (2H, m), 2.04–2.13 (8H, m), 2.27–2.31 (2H, m), 2.31–2.35 (2H, m), 6.95 (4H, d, $J = 8.1$ Hz), 7.21 (4H, d, $J = 8.1$ Hz) ppm. $^{13}\text{C NMR } \delta$ (75 MHz, CDCl_3): 27.7, 31.0, 35.2, 37.8, 39.5, 41.3, 42.5, 120.8, 127.8, 147.8, 148.7, 175.3 ppm. IR ν (neat): 1748 cm^{-1} . Anal. Calcd. for $\text{C}_{27}\text{H}_{28}\text{O}_4$: C 77.86%, H 6.78%. Found, C 77.22%, H 6.51%.

Polyester 10d: $^1\text{H NMR } \delta$ (300 MHz, CDCl_3): 1.89–1.93 (2H, m), 2.03–2.16 (8H, m), 2.30–2.34 (2H, m), 2.34–2.39 (2H, m), 7.10 (4H, d, $J = 8.7$ Hz), 7.40 (4H, d, $J = 8.7$ Hz) ppm.

^{13}C NMR δ (75 MHz, CDCl_3): 27.7, 35.1, 37.8, 39.6, 41.4, 63.8 (sept, $^2J_{\text{CF}}$, $J = 25$ Hz), 121.3, 124.0 (q, $^1J_{\text{CF}}$, $J = 287$ Hz), 130.5, 131.4, 151.3, 174.7 ppm. IR ν (neat): 1755 cm^{-1} . Anal. Calcd. for $\text{C}_{27}\text{H}_{22}\text{F}_6\text{O}_4$: C 61.83%, H 4.23%. Found, C 61.69%, H 4.13%.

Polyester **10e**: ^1H NMR δ (300 MHz, CDCl_3): 1.50–1.62 (6H, m), 1.71–1.85 (2H, m), 1.95–2.11 (8H, m), 2.20–2.29 (6H, m), 2.29–2.35 (2H, m), 6.96 (4H, d, $J = 8.7$ Hz), 7.24 (4H, d, $J = 8.7$ Hz) ppm. ^{13}C NMR δ (75 MHz, CDCl_3): 22.7, 26.1, 27.7, 35.2, 37.2, 37.7, 39.4, 41.2, 45.6, 120.9, 128.0, 145.6, 148.4, 175.1 ppm. IR ν (neat): 1747 cm^{-1} . Anal. Calcd. for $\text{C}_{30}\text{H}_{32}\text{O}_4$: C 78.92%, H 7.06%. Found, C 79.16%, H 6.99%.

RESULTS AND DISCUSSION

Polymerization of *trans*-1,2-Cyclohexanedicarbonyl Dichloride (**2**) with 4,4'-Oxybiphenol (**3a**)

trans-1,2-Cyclohexanedicarbonyl dichloride (**2**) was prepared through the reaction of *trans*-1,2-cyclohexanedicarboxylic acid (**1**) with PCl_5 at room temperature.¹³

First, solution polycondensation of diacyl dichloride **2** with 4,4'-oxybiphenol (**3a**)¹⁴ in the presence of triethylamine was attempted under various reaction conditions. However, only low-molecular-weight polyester **4a** was obtained in low yield (*ca.* 70%). In particular, polycondensation at higher temperature afforded lower-molecular-weight polyester. Probably, reverse reaction, *i.e.*, base-mediated hydrolysis of the resulting polyesters, proceeds in this homogeneous system.

Next, interfacial polycondensation⁶ of diacyl dichloride **2** with 4,4'-oxybiphenol (**3a**) in aqueous $\text{NaOH}/\text{CHCl}_3$ was performed at room temperature. The results are shown in Table I.

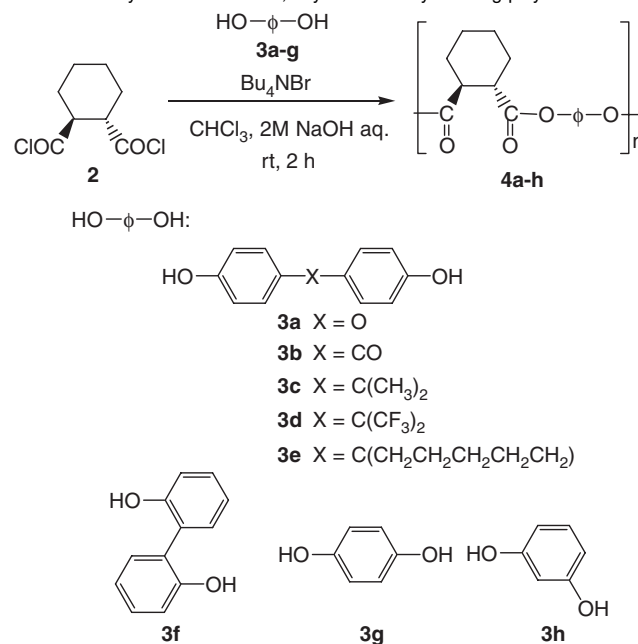
When polycondensation of dichloride **2** with **3a** in 2 M aqueous $\text{NaOH}/\text{CHCl}_3$ ($v/v = 2/1$) was performed, the highest-molecular-weight polyester (**4a**, $M_n = 38000$) was obtained (Run 4). M_n of the polyester which was obtained in 1 M aqueous $\text{NaOH}/\text{CHCl}_3$ was lower because of decrease in the rate of polymerization (Run 1). On the other hand, M_n of the polyester obtained in 3 M aqueous $\text{NaOH}/\text{CHCl}_3$, was also lower because of progress of reverse reaction, *i.e.*, ester hydrolysis (Run 2). Control of concentration of aqueous NaOH is also essential to smooth polycondensation (Runs 1–3). In addition, addition of the phase-transfer catalyst is effective to promote polycondensation (Runs 2 and 6).

Table I. Interfacial polycondensation of *trans*-1,2-cyclohexanedicarbonyl dichloride (**2**) with 4,4'-oxybiphenol (**3a**)

Run	$\text{H}_2\text{O}/\text{mL}$	NaOH/mmol	CHCl_3/mL	$\text{Bu}_4\text{NBr}/\text{mmol}$	Yield/%	M_n^a
1	1.5	1.5 (1 mol/L)	0.25	0.025	93	9000
2	0.75	1.5 (2 mol/L)	0.25	0.025	90	13100
3	0.5	1.5 (3 mol/L)	0.25	0.025	69	2300
4	0.5	1.0	0.25	0.025	90	38000
5	0.75	1.5	0.50	0.025	76	9100
6	0.75	1.5	0.25	0	34	<500

Reaction conditions: monomer **2**, 0.5 mmol; diol **3a**, 0.5 mmol, rt, 2 h. a) Estimated by GPC (eluent; CHCl_3) based on polystyrene standards.

Table II. Synthesis of *trans*-1,2-cyclohexanediyl-bearing polyesters **4a-h**



Run	Monomer	2 M NaOH aq./mL	Yield/%	M_n^a	$T_g/^\circ\text{C}^b$	$T_{d5}/^\circ\text{C}^c$
1	3a	0.5	90 (4a)	38000	110	373
2	3b	0.5	92 (4b)	22000	134	351
3	3c	0.7	95 (4c)	85000	140	376
4	3d	0.5	61 (4d)	8000	156	351
5	3e	1.0	65 (4e)	8000	156	314
6	3f	0.5	9 (4f)	— ^d	— ^d	— ^d
7	3g	0.5	22 (4g)	— ^d	— ^d	— ^d
8	3h	0.5	36 (4h)	— ^d	— ^d	— ^d

Reaction conditions: monomer **2**, 0.5 mmol; diol **3**, 0.5 mmol; Bu_4NBr , 0.025 mmol; CHCl_3 , 0.25 mL; 2 M NaOH aq.; rt, 2 h. a) Estimated by GPC (eluent; CHCl_3) based on polystyrene standards. b) Determined on the basis of DSC curves. Heating rate: 10 K/min. c) Temperature where a 5% weight loss occurs. Heating rate: 10 K/min. d) Not measured.

Polymerization of *trans*-1,2-Cyclohexanedicarbonyl Dichloride (**2**) with Several Aromatic Diols **3a-h**

The results of polycondensation of *trans*-1,2-cyclohexanedicarbonyl dichloride (**2**) with several aromatic diols **3a-h** are shown in Table II. In the polymerization of aromatic diols **3c** and **3e**, more amount of 2 M aqueous NaOH was required because of low solubility of diols **3c** and **3e**. High-molecular-weight polyesters **4a-e** were obtained when bisphenols **3a-e** were employed. On the other hand, polyesters **4f-h** were obtained in low yields when 2,2'-biphenol (**3f**), hydroquinone (**3g**), and resorcinol (**3h**) were employed. As aromatic diols, bisphenols **3a-e** are suitable to promote polymerization because σ -bond units located between two phenolic units give moderate flexibility to the main chains and solubility of the resulting oligomers in CHCl_3 is maintained. In addition, decrease of π -conjugation by introduction of σ -bond units affects maintenance of reactivity, *i.e.*, nucleophilicity of phenoxide. M_n 's of polyesters **4d-e** are relatively lower than those of polyesters **4a-c**, which is caused by precipitation of the polyesters (**4d-e**) at the early stage of polymerization.

Table III. Synthesis of *trans*-1,4-cyclohexanediyl-bearing polyesters **7a-e**

Run	Monomer	2M NaOH aq./mL	Yield/%	M_n^a	$T_g/^\circ\text{C}^b$	$T_{d5}/^\circ\text{C}^c$
1	3a	0.5	73 (7a)	— ^d	121	330
2	3b	0.5	73 (7b)	— ^d	125	304
3	3c	0.7	87 (7c)	12000	157	309
4	3d	0.5	74 (7d)	13000	163	355
5	3e	1.5	83 (7e)	— ^d	174	325

Reaction conditions: monomer **6**, 0.5 mmol; diol **3**, 0.5 mmol; Bu_4NBr , 0.025 mmol; 2 M aqueous NaOH, 0.50 mL; CHCl_3 , 0.25 mL; 2 M NaOH aq.; rt, 2 h. a) Estimated by GPC (eluent; CHCl_3) based on polystyrene standards. b) Determined on the basis of DSC curves. Heating rate: 10 K/min. c) Temperature where a 5% weight loss occurs. Heating rate: 10 K/min. d) Not measured. The resulting polyesters **7a**, **7b**, and **7e** were insoluble in CHCl_3 .

Polymerization of *trans*-1,4-Cyclohexanedicarbonyl Dichloride (**6**) with Aromatic Diols **3a-e**

Similarly, interfacial polycondensation of regioisomeric dicarbonyl dichloride, *i.e.*, *trans*-1,4-cyclohexanedicarbonyl dichloride¹⁵ (**6**) with bisphenols **3a-e** were carried out. The results are shown in Table III. Polyesters **7a**, **7b**, and **7e** were partly insoluble in CHCl_3 . This means that *trans*-1,4-cyclohexanediyl units where two substituents are situated at equatorial positions symmetrically are more rigid than *trans*-1,2-cyclohexanediyl ones. DSC measurement disclosed that T_g 's of polyesters **7** are higher than those of polyesters **4**. On the contrary, TG measurement disclosed that thermal degradation of polyesters **4** starts to occur at higher temperatures than that of polyesters **7**. Thermal bond cleavages of polyesters **4** are harder to occur than those of polyesters **7** because 1,2-cyclohexanediyl units are more bulky than 1,4-cyclohexanediyl ones, probably.

Polymerization of 1,3-Adamantanedicarbonyl Dichloride (**9**) with Aromatic Diols **3a-e**

Polycondensation of 1,3-adamantanedicarbonyl chloride (**9**)¹⁶ with bisphenols **3a-e** were also examined. The results are shown in Table IV.

Polyesters **10a**, **b**, and **e** are soluble in typical organic solvents. These polyester films are obtained by casting from CHCl_3 . Generally, polyesters **10** are slightly less soluble than polyesters **4** but much more soluble than polyesters **7** (Table V).

T_g 's of polyesters **10** are higher than those of polyesters **4** and **7**. Figure 1 shows TG thermograms of polyesters **4a**, **7a**, and **10a**. Thermal degradation of polyesters **10** starts to occur at higher temperatures than that of polyesters **4** and **7**.

Table IV. Synthesis of 1,3-adamantanediyl-bearing polyesters **10a-e**

Run	Monomer	2M NaOH aq./mL	Yield/%	M_n^a	$T_g/^\circ\text{C}^b$	$T_{d5}/^\circ\text{C}^c$
1	3a	0.5	87 (10a)	22000	184	425
2	3b	0.5	97 (10b)	21000	188	405
3	3c	0.7	87 (10c)	7000	203	428
4	3d	0.5	83 (10d)	— ^d	205	396
5	3e	1.5	99 (10e)	21000	222	448

Reaction conditions: monomer **9**, 0.5 mmol; diol **3**, 0.5 mmol; Bu_4NBr , 0.025 mmol; CHCl_3 , 0.25 mL; 2 M NaOH aq.; rt, 2 h. a) Estimated by GPC (eluent; CHCl_3) based on polystyrene standards. b) Determined on the basis of DSC curves. Heating rate: 10 K/min. c) Temperature where a 5% weight loss occurs. Heating rate: 10 K/min. d) Not measured. Polymer **10d** was insoluble in CHCl_3 .

Table V. Solubility of polyesters **4**, **7**, and **10**

Polymer	CHCl_3	<i>m</i> -cresol	THF	DMSO	DMF	DMAc	NMP	H_2SO_4
4a	++	+	++	++	++	++	++	++
4b	++	++	++	+	++	±	++	++
4c	++	++	±	±	±	++	++	++
4d	±	+	±	±	±	±	—	++
4e	±	++	±	—	±	±	±	++
7a	—	±	—	—	—	—	—	++
7b	—	±	—	—	—	—	—	++
7c	±	±	—	±	±	—	±	++
7d	±	—	±	±	±	—	±	++
7e	—	±	—	—	—	—	±	++
10a	++	+	++	—	++	++	++	++
10b	++	±	++	—	++	++	++	++
10c	±	±	—	±	—	—	±	++
10d	+	±	—	±	—	—	±	++
10e	++	+	—	—	—	—	±	++

Solubility: (++): soluble at room temperature. (+): soluble upon heating. (±): partially soluble or swelling. (—): insoluble.

Finally, UV-vis transmittance spectra of the polyester flexible films **10a,b,e**, which were prepared by casting from CHCl_3 , are shown in Figure 2. Little absorption is observed in the wavelength above 300 nm for polyesters **10a** and **10e**. The cutoff wavelengths of these polyesters are shorter than those of wholly aromatic polyesters (~350 nm).⁴ Introduction of bulky and non-conjugated alicyclic units and bisphenols probably improves the transparency to the polyesters.

CONCLUSIONS

Aromatic polyesters containing alicyclic units were synthesized through interfacial polycondensation of alicyclic dicarbonyl chlorides and bisphenols in 2 M aqueous NaOH/ CHCl_3 .

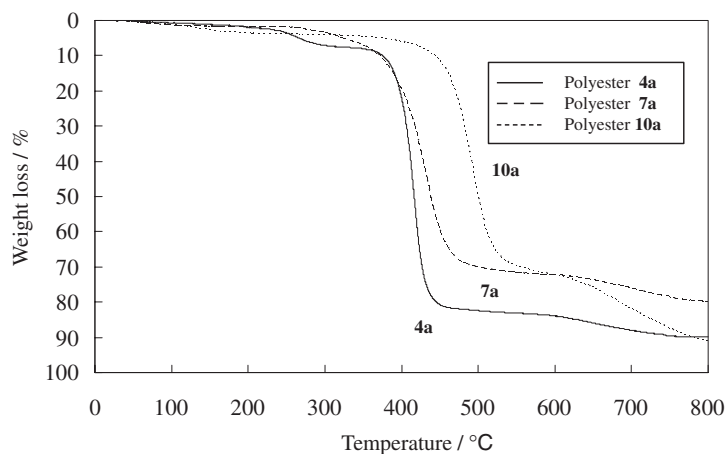


Figure 1. TG thermograms of polyesters 4a, 7a, and 10a.

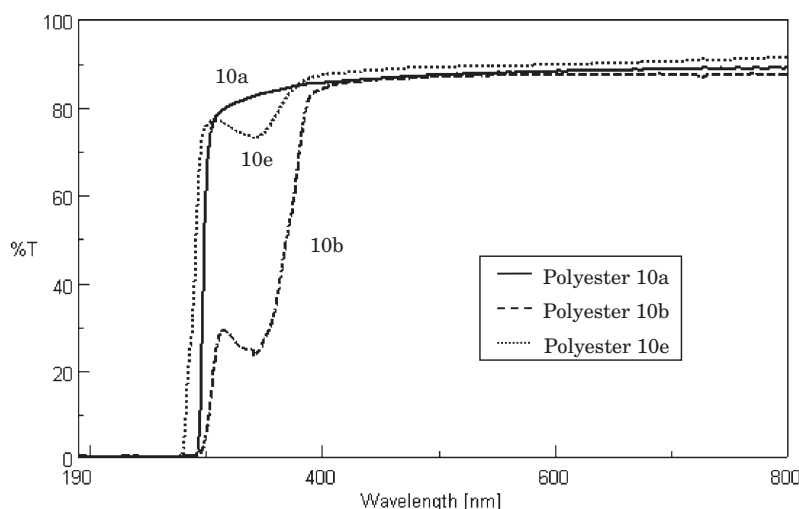


Figure 2. UV-vis transmittance spectra of polyesters 10a, b, and e.

Almost of the resulting polyesters **4** and **10** exhibit excellent thermal stability, solubility in organic solvents, and transparency. In particular, polyesters **10** have excellent chemical and physical properties.

Now, we have been studying the application of these polyesters to optical and electrical materials.

Acknowledgment. This work is supported from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

Received: March 6, 2008
Accepted: March 26, 2008
Published: May 21, 2008

REFERENCES

1. T. Yasuda, *Kogyo Zairyo*, **55**, 18 (2007).
2. T. Watanabe, *Gekkan Display*, 47 (2003).
3. V. V. Korshak and S. V. Vinogradova, "Polyesters," Pergamon Press, 1965.
4. K. Imanishi, *Kino Zairyo*, **27**, 30 (2007).
5. T. Oyama, A. Kitamura, T. Fukushima, T. Iijima, and M. Tomoi, *Macromol. Rapid Commun.*, **23**, 104 (2002).
6. T. Oyama, A. Kitamura, E. Sato, and M. Tomoi, *J. Polym. Sci., Part A: Polym. Chem.*, **44**, 2694 (2006).
7. T. Matumoto, *J. Synth. Org. Chem. Jpn.*, **58**, 776 (2000).
8. Q. Jin, T. Yamashita, K. Horie, R. Yokota, and I. Mita, *J. Polym. Sci., Part A: Polym. Chem.*, **31**, 2345 (1993).
9. H. Seino, A. Mochizuki, and M. Ueda, *J. Polym. Sci. Part A: Polym. Chem.*, **37**, 3584 (1999).
10. K. Fukukawa, Y. Shibasaki, and M. Ueda, *Macromolecules*, **37**, 8256 (2004).
11. K. Obuchi, M. Komatsu, and K. Minami, *Proceedings of APIE-The International Society for Optical Engineering*, 6671 (2001).
12. N. Nishimura, K. Maeyama, and A. Toyota, *Progress in Olefin Polymerization Catalysts and Polyolefin Materials*, 193 (2006).
13. B. P. Dervan and R. C. Jones, *J. Org. Chem.*, **44**, 2116 (1979).
14. K. Maeyama, I. Hikiji, K. Ogura, A. Okamoto, K. Ogino, H. Saito, and N. Yonezawa, *Polym. J.*, **37**, 736 (2005).
15. F. Higashi and S. Sugimori, *Macromol. Rapid Commun.*, **21**, 891 (2000).
16. T. D. Dang, M. J. Dalton, N. Venkatasubramanian, J. A. Johnson, C. A. Cerbus, and W. A. Feld, *J. Polym. Sci., Part A: Polym. Chem.*, **42**, 6134 (2004).