Convenient Synthesis of Aromatic Poly(ether ketone)s Containing Alicyclic Units

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Aromatic poly(ether ketone)s containing cyclohexanediyl and adamantanediyl units were synthesized through nucleophilic aromatic substitution polymerization of alicyclic difluorides with bisphenols in the presence of K_2CO_3 in NMP. Most of the poly(ether ketone)s thus synthesized are soluble in organic solvents such as $CHCl_3$ and THF. Glass transition temperatures (T_g 's) of the polymers and temperatures where 5% weight losses occur are in the region of 146–199 °C and 432–500 °C, respectively, which shows that the poly(ether ketone)s have excellent thermal stability. UV spectra of the poly(ether ketone)s revealed that they are sufficiently transparent in the wavelength above 310 nm.

KEY WORDS: Semi-aromatic Poly(ether ketone)s / Nucleophilic Aromatic Substitution Polymerization / Thermal Stability / Excellent Solubility /

Aromatic poly(ether ketone)s, which consists of aromatics, ketone groups, and ether units, have much attraction as physically and chemically stable organic materials.^{1,2} In particular, PEEK has been well-known as one of super engineering plastics. We have also synthesized aromatic poly(ether ketone)s^{3,4} and wholly aromatic polyketones⁵ containing optically active 2,2'-dimethoxy-1,1'-binaphthyl-6,6'-diyl units. The resulting polymers have high thermal stability and excellent solubility in organic solvents such as $CHCl_3$ and DMF. On the other hand, polyimides,^{6–8} poly(benzoxazole)s,⁹ and polyolefins^{10,11} incorporating alicyclic units derived from norbornene and adamantane derivatives have been recently much reported. Incorporation of alicyclic units to aromatic polymer skeletons increases transparency associating with small decrease of thermal stability. We have also synthesized semi-aromatic polyesters incorporating alicyclic units, *i.e.*, cyclohexanediyl and adamantanediyl ones, in the main chains.¹² The resulting polyesters have also high thermal stability (T_g 222 °C) and excellent solubility in organic solvents such as $CHCl_3$ and DMF as well as good transparency. These motivated us to develop poly(ether ketone)s consisting of both aromatic and alicyclic units, which should be applied to high-performance materials including optical materials.

In this paper, we report synthesis of poly(ether ketone)s through nucleophilic aromatic substitution polymerization of difluorides containing alicyclic units with bisphenols in the presence of K_2CO_3 . Thermal and optical properties and solubility in organic solvents of the resulting poly(ether ketone)s are also described.

EXPERIMENTAL

Materials

Cyclohexanedicarboxylic acids, fluorobenzene, aromatic diols **5c,d**, and PCl_5 were purchased from Tokyo Kasei Kogyo

Co. Ltd. Aromatic diols **5a,b** were purchased from Wako Pure Chemical Industries. A THF solution of 4-fluorophenylmagnesium bromide was purchased from Aldrich. These reagents were used as received. DMF and NMP were purchased from Kanto Chemical Co. Ltd. and used after distillation under reduced pressure. Cyclohexanedicarbonyl dichlorides **1** and **3** were prepared through the reaction of the corresponding cyclohexanedicarboxylic acid with PCl_5 at room temperature.¹² On the other hand, 1,3-adamantanedicarbonyl dichloride (**8**) was prepared through the reaction of 1,3-adamantanedicarboxylic acid with $SOCl_2$.

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 Me_4Si (δ , 0.00). ^{13}C NMR spectra were recorded on a JEOL JNM-AL-300 (75 MHz). Chemical shifts were expressed in ppm relative to internal standard of $CDCl_3$ (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 $CHCl_3$ 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 obtained on the basis of DSC thermograms. DSC thermograms 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 obtained on the basis of TGA thermograms. The TGA thermograms were recorded on a Rigaku TG-8120 thermogravimeter with a heating rate of $10 K min^{-1}$. UV spectra were recorded on a JEOL V-630 spectrophotometer.

trans-1,2-Bis(4-fluorobenzoyl)cyclohexane (**2**)

To a dried 30 mL two-necked flask were added *trans*-1,2-

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cyclohexanedicarbonyl dichloride (**1**, 212 mg, 2 mmol), aluminium chloride (668 mg, 5 mmol), and 1,2-dichloroethane (6 mL). After the mixture was stirred for several minutes at 0 °C, fluorobenzene (1.15 g, 12 mmol) was added. The reaction mixture was stirred for 24 h at room temperature. The reaction mixture was quenched by pouring it into saturated NaHCO₃ aq. in a beaker. The organic layer was extracted with chloroform three times. The combined extracts were dried over anhydrous MgSO₄. After removal of the drying agent, chloroform was removed under reduced pressure. The crude product was purified by recrystallization from hexane/CHCl₃ to afford pure difluoride **2** in 65% yield.

Melting point 135–136 °C. ¹H NMR δ (300 MHz, CDCl₃): 1.31–1.59 (4H, m), 1.85–1.98 (2H, m), 2.02–2.15 (2H, m), 3.75–3.95 (2H, m), 7.13 (4H, t, *J* = 9.0 Hz), 8.01 (4H, dd, *J* = 5.4, 9.0 Hz) ppm. ¹³C NMR δ (75 MHz, CDCl₃): 25.9, 30.1, 47.1, 115.7 (d, ²*J*_{CF} = 22 Hz), 131.1 (d, ³*J*_{CF} = 9 Hz), 132.5 (d, ⁴*J*_{CF} = 3 Hz), 165.7 (d, ¹*J*_{CF} = 253 Hz), 201.8 ppm. IR ν(neat) 1673 cm⁻¹. Anal. Calcd. for C₂₀H₁₈F₂O₂: C 73.16%, H 5.53%. Found, C 73.39%, H 5.68%.

trans-1,4-Bis(4-fluorobenzoyl)cyclohexane (**4**)

trans-1,4-Bis(4-fluorobenzoyl)cyclohexane (**4**) was prepared according to the synthesis of *trans*-1,2-bis(4-fluorobenzoyl)cyclohexane (**2**). Isolated yield, 78%.

Melting point 208–213 °C. ¹H NMR δ (300 MHz, CDCl₃): 1.64–1.78 (4H, m), 1.95–2.19 (4H, m), 3.22–3.37 (2H, m), 7.16 (4H, t, *J* = 8.4 Hz), 7.99 (4H, dd, *J* = 5.1, 8.4 Hz) ppm. ¹³C NMR δ (75 MHz, CDCl₃): 28.6, 44.7, 115.7 (d, ²*J*_{CF} = 26 Hz), 130.8 (d, ³*J*_{CF} = 9 Hz), 132.3 (d, ⁴*J*_{CF} = 3 Hz), 165.7 (d, ¹*J*_{CF} = 253 Hz), 201.8 ppm. IR ν(neat) 1679 cm⁻¹. Anal. Calcd. for C₂₀H₁₈F₂O₂: C 73.16%, H 5.53%. Found, C 73.39%, H 5.64%.

1,3-Bis(4-fluorobenzoyl)adamantane (**9**)

To a dried 30 mL two-necked flask were added 1,3-adamantanedicarbonyl dichloride (**8**, 391 mg, 1.5 mmol), CuCl¹³ (10 mg, 0.075 mmol), and THF (4 mL). After the mixture was stirred for several minutes at 0 °C, a 1 M THF solution of 4-fluorophenylmagnesium bromide (3.5 mL) was added dropwise. The reaction mixture was quenched by pouring it into 1 M HCl aq. in a beaker. The organic layer was extracted with diethyl ether three times. The combined extracts were dried over anhydrous MgSO₄. After removal of the drying agent, diethyl ether was removed under reduced pressure. The crude product was purified by recrystallization from CHCl₃/hexane to afford pure difluoride **9** in 70% yield.

Melting point 118–120 °C. ¹H NMR δ (300 MHz, CDCl₃): 1.73–1.80 (2H, m), 1.90–2.15 (8H, m), 2.19–2.39 (4H, m), 7.09 (4H, t, *J* = 8.7 Hz), 7.65 (4H, dd, *J* = 5.1, 8.7 Hz) ppm. ¹³C NMR δ (75 MHz, CDCl₃): 28.1, 35.5, 38.3, 40.3, 47.2, 115.2 (d, ²*J*_{CF} = 22 Hz), 130.0 (d, ³*J*_{CF} = 9 Hz), 134.6 (d, ⁴*J*_{CF} = 4 Hz), 164.0 (d, ¹*J*_{CF} = 250 Hz), 206.6 ppm. IR ν(neat) 1660 cm⁻¹. Anal. Calcd. for C₂₄H₂₂F₂O₂: C 75.77%, H 5.83%. Found, C 75.81%, H 6.01%.

Synthesis of Poly(ether ketone)s **6**, **7**, and **10**

To a 10 mL one-necked flask equipped with a reflux condenser were added difluoride **2/4/9** (0.5 mmol), bisphenol **5** (0.5 mmol), potassium carbonate (1.5 mmol), freshly distilled NMP (1 mL). The NMP solution was stirred at 140 °C for 1 h and further stirred at 170 °C for 7 h. The reaction mixture was poured into methanol and the resulting solid was collected by filtrate suction. The collected solid was washed with water and methanol three times to afford the corresponding poly(ether ketone) **6/7/10**.

Poly(ether ketone) **6a**: ¹H NMR δ (300 MHz, CDCl₃): 1.25–1.53 (4H, m), 1.71 (6H, s), 1.75–1.95 (2H, m), 2.01–2.19 (2H, m), 3.78–3.91 (2H, m), 6.80–7.15 (8H, m), 7.18–7.30 (4H, m), 7.89–8.08 (4H, m). ¹³C NMR δ (75 MHz, CDCl₃): 25.9, 30.3, 31.0, 42.3, 46.9, 117.3, 119.5, 128.2, 130.6, 130.7, 146.7, 153.4, 161.9, 202.0 ppm. IR ν (KBr): 1673 cm⁻¹. Anal. Calcd. for C₃₅H₃₂O₄: C 81.37%, H 6.24%. Found, C 81.35%, H 6.51%.

Poly(ether ketone) **6b**: ¹H NMR δ (300 MHz, CDCl₃): 1.31–1.50 (4H, m), 1.85–1.99 (2H, m), 2.08–2.19 (2H, m), 3.78–3.92 (2H, m), 6.98–7.11 (8H, m), 7.32–7.45 (4H, m), 7.97–8.07 (4H, m) ppm. ¹³C NMR δ (75 MHz, CDCl₃): 25.9, 30.3, 47.0, 63.8, (sept, ²*J*_{CF} = 26 Hz), 118.5, 118.9, 124.1 (q, ¹*J*_{CF} = 292 Hz), 128.7, 130.9, 131.6, 131.9, 156.6, 160.5, 202.0 ppm. IR ν (KBr): 1676 cm⁻¹. Anal. Calcd. for C₃₅H₂₆F₆O₄: C 67.31%, H 4.20%. Found, C 67.07%, H 4.48%.

Poly(ether ketone) **6c**: ¹H NMR δ (300 MHz, CDCl₃): 1.19–1.71 (10H, m), 1.73–1.93 (2H, m), 1.99–2.18 (2H, m), 2.20–2.40 (4H, m), 3.71–3.88 (2H, m), 6.81–7.11 (8H, m), 7.14–7.35 (4H, m), 7.85–8.09 (4H, m) ppm. ¹³C NMR δ (75 MHz, CDCl₃): 22.8, 25.9, 26.1, 30.2, 37.3, 45.5, 46.9, 117.3, 119.6, 128.6, 130.6, 130.7, 144.6, 153.1, 161.8, 201.9 ppm. IR ν (KBr): 1673 cm⁻¹. Anal. Calcd. for C₃₈H₃₆O₄: C 81.99%, H 6.52%. Found, C 81.62%, H 6.57%.

Poly(ether ketone) **6d**: ¹H NMR δ (300 MHz, CDCl₃): 1.48–1.59 (4H, m), 1.85–1.93 (2H, m), 2.09–2.20 (2H, m), 3.81–3.92 (2H, m), 6.94–7.02 (4H, m), 7.05–7.09 (8H, m), 7.97–8.02 (4H, m) ppm. ¹³C NMR δ (75 MHz, CDCl₃): 25.9, 30.2, 46.9, 116.9, 120.1, 121.6, 130.6, 130.8, 150.9, 153.9, 162.1, 201.9 ppm. IR ν (KBr): 1672 cm⁻¹. Anal. Calcd. for C₃₂H₂₆O₅: C 78.35%, H 5.34%. Found, C 77.90%, H 5.22%.

Poly(ether ketone) **7a**: ¹H NMR δ (300 MHz, CDCl₃): 1.50–1.79 (6H, m), 1.94–2.11 (4H, m), 2.22–2.36 (4H, m), 3.22–3.34 (2H, m), 6.92–7.03 (8H, m), 7.29–7.33 (4H, m), 7.89–7.95 (4H, m) ppm. ¹³C NMR δ (75 MHz, CDCl₃): 28.7, 31.0, 42.3, 44.6, 117.2, 119.5, 128.3, 130.4, 130.5, 146.8, 153.2, 162.0, 201.8 ppm. IR ν (KBr): 1677 cm⁻¹. Anal. Calcd. for C₃₅H₃₂O₄: C 81.37%, H 6.24%. Found, C 81.46%, H 6.52%.

Poly(ether ketone) **7b**: ¹H NMR δ (300 MHz, CDCl₃): 1.63–1.79 (4H, m), 1.97–2.19 (4H, m), 3.22–3.38 (2H, m), 7.02–7.12 (8H, m), 7.37–7.44 (4H, m), 7.96–8.03 (4H, m) ppm. ¹³C NMR δ (75 MHz, CDCl₃): 28.7, 44.7, 63.8 (sept, ²*J*_{CF} = 25 Hz), 118.5, 118.9, 124.1 (q, ¹*J*_{CF} = 286 Hz), 128.7, 130.8, 131.5, 131.9, 156.5, 160.5, 201.5 ppm. IR ν (KBr): 1683 cm⁻¹. Anal. Calcd. for C₃₅H₂₆F₆O₄: C 67.31%, H 4.20%. Found, C 67.33%, H 4.47%.

Scheme 1. Preparation of monomers 2, 4, and 9.

Poly(ether ketone) **7c**: ^1H NMR δ (300 MHz, CDCl_3): 1.63–1.85 (14H, m), 1.93–2.12 (4H, m), 3.24–3.36 (2H, m), 6.97–7.07 (8H, m), 7.27–7.33 (4H, m), 7.91–7.99 (4H, m) ppm. ^{13}C NMR δ (75 MHz, CDCl_3): 22.8, 26.3, 28.7, 37.3, 44.6, 45.6, 117.3, 119.6, 119.7, 128.7, 130.5, 144.8, 153.0, 161.9, 201.8 ppm. IR ν (KBr): 1677 cm^{-1} . Anal. Calcd. for $\text{C}_{38}\text{H}_{36}\text{O}_4$: C 81.99%, H 6.52%. Found, C 81.55%, H 6.62%.

Poly(ether ketone) **7d**: Insoluble. IR ν (KBr): 1672 cm^{-1} . Anal. Calcd. for $\text{C}_{32}\text{H}_{26}\text{O}_5$: C 78.35%, H 5.34%. Found, C 78.24%, H 5.43%.

Poly(ether ketone) **10a**: ^1H NMR δ (300 MHz, CDCl_3): 1.69 (6H, s), 1.77 (2H, s), 1.95–2.13 (8H, m), 2.23–2.34 (4H, m), 6.95 (8H, d, $J = 8.7\text{ Hz}$), 7.24 (4H, d, $J = 8.7\text{ Hz}$), 7.70 (4H, d, $J = 8.7\text{ Hz}$) ppm. ^{13}C NMR δ (75 MHz, CDCl_3): 28.3, 31.0, 35.5, 38.6, 40.7, 42.3, 47.2, 117.0, 119.4, 128.2, 130.2, 132.5, 146.5, 153.5, 160.1, 206.2 ppm. IR ν (KBr): 1663 cm^{-1} . Anal. Calcd. for $\text{C}_{39}\text{H}_{36}\text{O}_4$: C 82.37%, H 6.38%. Found, C 82.44%, H 6.57%.

Poly(ether ketone) **10b**: ^1H NMR δ (300 MHz, CDCl_3): 1.78 (2H, s), 1.95–2.15 (8H, m), 2.30 (4H, s), 6.92–7.13 (8H, m), 7.39 (4H, d, $J = 8.1\text{ Hz}$), 7.72 (4H, d, $J = 8.1\text{ Hz}$) ppm. ^{13}C NMR δ (75 MHz, CDCl_3): 28.2, 35.5, 38.4, 40.5, 47.2, 64.2 (sept, $^2J_{\text{CF}} = 30\text{ Hz}$), 118.2, 118.6, 123.8(m), 128.5, 130.1, 131.9, 133.7, 156.8, 158.5, 206.5 ppm. IR ν (KBr): 1667 cm^{-1} . Anal. Calcd. for $\text{C}_{39}\text{H}_{30}\text{F}_6\text{O}_4$: C 69.23%, H 4.47%. Found, C 69.41%, H 4.51%.

Poly(ether ketone) **10c**: ^1H NMR δ (300 MHz, CDCl_3): 1.45–1.61 (10H, m), 1.77 (2H, s), 1.95–2.15 (8H, m), 2.21–2.34 (4H, m), 6.89–6.99 (8H, m), 7.22–7.30 (4H, m), 7.70 (4H, d, $J = 8.7\text{ Hz}$) ppm. ^{13}C NMR δ (75 MHz, CDCl_3): 22.8, 26.3, 28.4, 35.5, 37.3, 38.6, 40.7, 45.6, 47.3, 117.1, 119.5, 128.6, 130.2, 132.5, 144.5, 153.3, 160.1, 206.3 ppm. IR ν (KBr): 1664 cm^{-1} . Anal. Calcd. for $\text{C}_{42}\text{H}_{40}\text{O}_4$: C 82.86%, H 6.62%. Found, C 82.96%, H 6.76%.

Poly(ether ketone) **10d**: ^1H NMR δ (300 MHz, CDCl_3): 1.78 (2H, s), 1.95–2.15 (8H, m), 2.31 (4H, s), 6.95 (4H, d, $J = 8.7\text{ Hz}$), 7.00–7.08 (8H, m), 7.72 (4H, d, $J = 8.7\text{ Hz}$) ppm. ^{13}C NMR δ (75 MHz, CDCl_3): 28.3, 35.5, 38.6, 40.7, 47.2, 116.7, 120.1, 121.5, 130.2, 132.5, 151.1, 153.8, 160.4, 206.3

ppm. IR ν (KBr): 1662 cm^{-1} . Anal. Calcd. for $\text{C}_{36}\text{H}_{30}\text{O}_5$: C 79.68%, H 5.57%. Found, C 79.59%, H 5.80%.

RESULTS AND DISCUSSION

Synthesis of Poly(ether ketone)s 6 and 7

Two isomeric bis(4-fluorobenzoyl)cyclohexanes **2** and **4** were prepared through AlCl_3 -mediated regioselective Friedel-Crafts acylation reaction of cyclohexanedicarbonyl dichlorides **1** and **3** with fluorobenzene in 1,2-dichloroethane. Nucleophilic aromatic substitution polymerization of difluoride monomer **2** with bisphenol A (**5a**) was performed in the presence of K_2CO_3 in NMP. Low-molecular-weight poly(ether ketone) (**6a**) was obtained when the reaction mixture was stirred at 170°C at 8 h (Run 1). On the other hand, high-molecular-weight poly(ether ketone) (**6a**) was obtained when the reaction mixture was stirred at 140°C at 1 h and then 170°C at 7 h (Run 2). Probably, potassium diphenoxide is formed at 140°C and reacts with difluoride monomer **2** at 170°C to afford the corresponding poly(ether ketone).

The results of polymerization of difluoride **2** with bisphenols **5a–d** are shown in Table I.

The resulting poly(ether ketone)s (**6a–d**) were high-molecular-weight polymers on the basis of GPC measurements. In addition, poly(ether ketone)s **6a–d** have excellent solubility in organic solvents such as CHCl_3 and THF (Table IV). Introduc-

Table I. Polymerization of *trans*-1,2-bis(4-fluorobenzoyl)cyclohexane (**2**) with bisphenols **5a–d**

Run	Bisphenol	Yield/%	M_n^a	$T_g/^\circ\text{C}^b$	$T_{d5}/^\circ\text{C}^c$
1	5a ^d	65	3000	—	—
2	5a	93(6a)	18000	187	437
3	5b	97(6b)	20000	197	462
4	5c	92(6c)	15000	199	454
5	5d	100(6d)	12000	187	438

Reaction conditions: difluoride **2**, 0.5 mmol; bisphenol **5**, 0.5 mmol; potassium carbonate, 1.6 mmol; NMP, 1 mL; 140°C , 1 h then 170°C , 7 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) The reaction was performed at 170°C for 8 h.

Table II. Polymerization of *trans*-1,4-bis(4-fluorobenzoyl)cyclohexane (**4**) with bisphenols **5a-d**

Run	Bisphenol	Yield/%	M_n^a	$T_g/^\circ\text{C}^b$	$T_{d5}/^\circ\text{C}^c$
1	5a	89(7a)	19000	176	432
2	5b	99(7b)	14000	175	458
3	5c	87(7c)	18000	187	453
4	5d	93(7d)	insoluble	171	456

Reaction conditions: difluoride **4**, 0.5 mmol; bisphenol **5**, 0.5 mmol; potassium carbonate, 1.6 mmol; NMP, 1 mL; 140 °C, 1 h then 170 °C, 7 h.
a) Estimated by GPC (eluent; CHCl₃) 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.

Table III. Polymerization of 1,3-bis(4-fluorobenzoyl)adamantane (**9**) with bisphenols **5a-d**

Run	Bisphenol	Yield/%	M_n^a	$T_g/^\circ\text{C}^b$	$T_{d5}/^\circ\text{C}^c$
1	5a	99(10a)	35000	146	490
2	5b	67(10b)	8000	146	500
3	5c	98(10c)	13000	154	492
4	5d	99(10d)	28000	140	489

Reaction conditions: difluoride **9**, 0.5 mmol; bisphenol **5**, 0.5 mmol; potassium carbonate, 1.6 mmol; NMP, 1 mL; 140 °C, 1 h then 170 °C, 7 h.
a) Estimated by GPC (eluent; CHCl₃) 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.

Scheme 2. Synthesis of aromatic poly(ether ketone)s **6**, **7**, and **10**.

tion of *trans*-1,2-cyclohexanediyl units to poly(ether ketone) backbones might improve the solubility in organic solvents.

Similarly, nucleophilic aromatic substitution polymerization of regioisomeric difluoride monomer **4** with bisphenols **5a-d** was carried out. The results are shown in Table II. Although poly(ether ketone)s **7a-c** are soluble to organic solvents, polyketone **7d**, which is derived from 4,4'-oxybiphenol, is insoluble to CHCl₃. Glass transition temperatures (T_g 's) of poly(ether ketone)s **7a-d** are as high as those of polyketones **6a-d**. Temperatures where 5% weight losses occur (T_{d5}) for poly(ether ketone)s **7a-d** are also as high as those of poly(ether ketone)s **6a-d**.

Synthesis of Adamantanediyl-containing Polyketones **10**

Friedel-Crafts acylation reaction of fluorobenzene with 1,3-adamantanedicarbonyl dichloride (**8**) was attempted to obtain

the corresponding difluoride (**9**). However, complex mixtures including difluoride **9** as the minor product were obtained due to bulkiness of adamantane units (Scheme 2). Difluoride **9** was prepared *via* the reaction of dicarbonyl dichloride **8** with 4-fluorophenylmagnesium bromide in the presence of CuCl (Scheme 2).¹³

Nucleophilic aromatic substitution polymerization of difluoride monomer **9** with bisphenols **5a-d** was carried out. The results are shown in Table III. Poly(ether ketone)s **10a**, **10c**, and **10d** were obtained as high-molecular-weight polymers in good yields. On the other hand, poly(ether ketone) **10b**, which is derived from CF₃-disubstituted bisphenol (**5b**), was obtained as a lower-molecular-weight polymer (M_n 8000) in lower yield. The reason might be due to both low reactivity of bisphenol **5b**, based on electron withdrawing effect by CF₃ groups, and bulkiness of 1,3-adamantanediyl units.

Table IV. Solubility of poly(ether ketone)s **6**, **7**, and **10**

Polymer	<i>m</i> -cresol	THF	CHCl ₃	DMSO	DMF	NMP	H ₂ SO ₄
6a	++	++	++	±	±	++	++
6b	+	++	++	±	++	++	++
6c	++	++	++	±	±	++	++
6d	++	++	++	±	++	++	++
7a	++	++	++	±	±	++	++
7b	±	++	++	±	±	++	++
7c	±	++	++	±	±	++	++
7d	–	±	–	–	±	±	++
10a	++	++	++	–	±	++	++
10b	++	++	++	–	±	++	++
10c	++	++	++	–	±	++	++
10d	++	++	++	–	±	++	++

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

We have reported that T_g 's of the polyesters containing 1,3-adamantanediyl units are 184–222 °C and higher than those of the polyesters containing 1,2-cyclohexanediyl units (110–156 °C).¹² On the other hand, T_g 's of poly(ether ketone)s **10**(Ad) are 140–154 °C and lower than those of poly(ether ketone)s **6** (1,2-Cy) and **7** (1,4-Cy) as shown in Table III. There is a possibility that the bent structures of 1,3-adamantanediyl units give flexibility to the main chains of poly(ether ketone)s **10**. This might decrease T_g 's of poly(ether ketone)s **10**. On the contrary, stronger interaction between ester groups might suppress the rotation based on the bent structures of 1,3-adamantanediyl units in the main chains of the polyesters, which increases T_g 's of the polyesters containing 1,3-adamantanediyl units.

Figure 1 shows TG thermograms of poly(ether ketone)s **6a**(1,2-Cy), **7a**(1,4-Cy), and **10a**(Ad). Temperatures where 5% weight losses occur (T_{d5}) for poly(ether ketone)s **10a–d** are in the region of 489–500 °C. T_{d5} 's of poly(ether ketone)s **10**(Ad)

Figure 1. TG thermograms of poly(ether ketone)s **6a**, **7a**, and **10a**. **Figure 2.** UV-vis spectra of poly(ether ketone)s **6a**, **7a**, and **10a**.

are higher than those of poly(ether ketone)s **6**(1,2-Cy) and **7**(1,4-Cy), probably due to bulkiness of adamantane units.

UV spectra of poly(ether ketone) films **6a**(1,2-Cy), **7a**(1,4-Cy), and **10a**(Ad), which are prepared by casting from CHCl₃, are shown in Figure 2. The spectra indicate that the films are transparent in wavelength above 310 nm.

CONCLUSIONS

Aromatic poly(ether ketone)s **6**, **7**, and **10** containing cyclohexanediyl and adamantanediyl units were synthesized through nucleophilic aromatic substitution polymerization of alicyclic difluorides **2**, **4**, and **9** with bisphenols **5a-d** in the presence of AlCl₃ in NMP. Most of poly(ether ketone)s **6**, **7**, and **10** have excellent thermal stability, solubility in organic solvents, and transparency.

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