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Polymerization of *α,ω*-Bis(*o*-methoxyphenyl)arenes with *trans*-1,4-Cyclohexanedicarboxylic acid: Yielding Organosoluble Semi-Aromatic Polyketones

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Abstract: A series of α,ω-bis(*o*-methoxyphenyl)arenes were prepared through Suzuki-Miyaura coupling reactions of dibromoarenes with *o*-methoxyphenyl boronic acid. P_2O_5-CH_3SO_3H-mediated direct polycondensation of α,ω-bis(*o*-methoxyphenyl)arenes with *trans*-1,4-cyclohexanedicarboxylic acid proceeded regioselectively to afford 1,4-cyclohexanediyl-containing aromatic polyketones. The resulting aromatic polyketones have high *Tg* and excellent solubility in typical organic solvents. In addition, the polyketone films fabricated by solution casting method are more colorless and transparent than those without cyclohexanediyl units.

Keywords: aromatic polyketones; α,ω-bis(*o*-methoxyphenyl)arenes; Suzuki-Miyaura coupling; thermal stability; transparency

1. Introduction

Aromatic polyketones such as poly(ether ether ketone)(PEEK) and poly(ether ketone ketone)(PEKK) have been attractive for their excellent physical and chemical stability as alternative materials to metals, which are applied for HPLC piping, airplanes, automobiles, fuel cells, and so on [1-3]. Almost of typical aromatic polyketones are ocher-colored and opaque. On the other hand, we have also reported aromatic polyketones with good heat-resistance and good solubility to typical organic solvents [4-14]. In addition, we have reported semi-aromatic polyketones *via* nucleophilic aromatic substitution polymerization of bis(4-fluorobenzoylated) alicyclic compounds with bisphenols. The resulting polyketones have good heat-resistance, good solubility to typical organic solvents, and moderate colorless transparency [15].

Electrophilic aromatic acyl-substitution reaction is general to connect an aromatic ring with a ketonic group. When an acyl group is introduced to an aromatic ring, no further acylation reaction on the ring proceeds because the introduced acyl group decreases the electron density of the ring, which leads to deactivation of the mono-acylated arene.

We have developed to synthesize aromatic polyketones by using acyl-acceptant monomers such as 2,2'-dimethoxybiphenyl and 2,2'-dimethoxy-1,1'-binaphthyl [4,10,11]. Two methoxy groups in these monomers increase the electron density of arenes. In addition, these monomers have non-coplanarity with large dihedral angles by steric hindrance between two *o*-substituted aromatic rings, which leads to reduction of resonance effects between two aromatic rings. Therefore, the reactivity at the second reactive site (5' position for 2,2'-dimethoxybiphenyl and 6' position for 2,2'-dimethoxy-1,1'-binaphthyl) is kept after the first acylation and sustainable polymerization proceeds. Incorporation of aromatic non-coplanar units to the main chains also contributes to excellent organosolubility of the resulting polyketones.

In our previous paper, we reported P_2O_5-CH_3SO_3H mediated polycondensation of *trans*-1,4-cyclohexanedicarboxylic acid with 2,2′-dialkoxybiphenyls, affording cyclohexanediyl-bearing aromatic polyketones [16]. Almost of the resulting polyketones have sufficient heat-resistance, organosolubility, and colorless transparency. However, the cyclohexanediyl-bearing aromatic polyketone derived from 2,2′-dimethoxybiphenyl and *trans*-1,4-cyclohexanedicarboxylic acid is insoluble in typical organic solvents such as $CHCl_3$. On the other hand, the cyclohexanediyl-bearing aromatic polyketone derived from 2,2′-*dipropyloxy*biphenyl and *trans*-1,4-cyclohexanedicarboxylic acid is soluble in typical organic solvents such as $CHCl_3$ and DMF. Introduction of noncoplanar units such as 2,2′-*dimethoxy*-5,5′-biphenylene is insufficient to solubilize the resulting polyketones. Introduction of longer alkoxy groups to acyl-acceptant monomers is effective to solubilize the resulting polyketones. However, the glass transition temperature(T_g) of the polyketone decreases drastically.

Two methoxy-substituted benzene rings of 2,2'-dimethoxybiphenyl are connected to each other with a large dihedral angle. This motivated us to develop novel acyl-acceptant monomers where two methoxy-substituted aromatic rings are connected through an aromatic linker (Figure 1). Introduction of aromatic linkers, which consist of bent and/or noncoplanar units, between two *o*-methoxyphenyl groups will improve the solubility of the resulting aromatic polyketones.

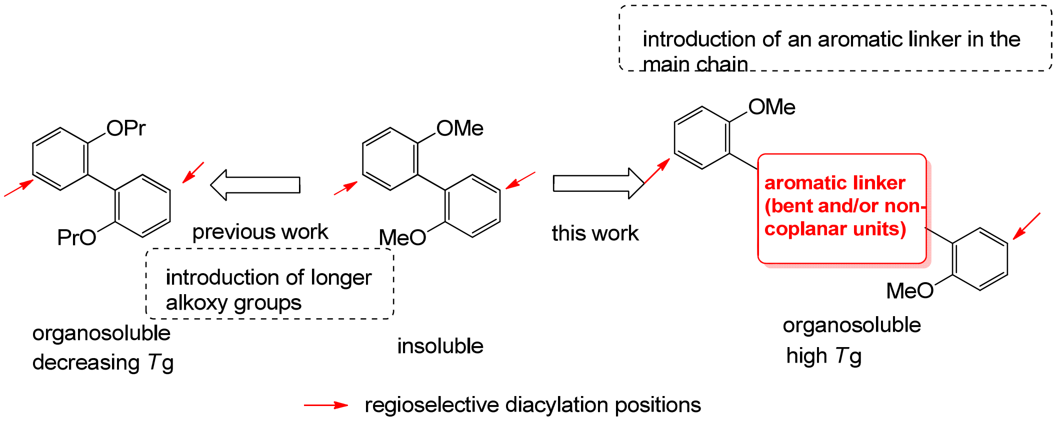


Figure 1. Concept of novel acyl-acceptant monomers in this work

In this article, we would like to report the facile preparation of five acyl-acceptant monomers (**3a-e**) *via* Suzuki-Miyaura coupling reaction and their application to effective and regioselective synthesis of aromatic polyketones bearing 1,4-cyclohexanedicarbonyl units through P_2O_5-MsOH-mediated direct condensation. The resulting polyketones **5a-e** have sufficiently high thermal stability and excellent organosolubility, and sufficient colorless transparency.

2. Materials and Methods

2.1. Materials

1,3-Dibromobenzene (**1a**), 1,2-dibromobenzene (**1b**), 1,3-dimethoxybenzene, 1,4-dimethoxybenzene, 2,2'-biphenol, *trans*-1,4-cyclohexanedicarboxylic acid (**4**), and methanesulfonic acid (MsOH) were purchased from Tokyo Chemical Industry Co., Ltd (>98%, Tokyo, Japan). Iodomethane, P_2O_5, and $Pd(PPh_3)_4$ were purchased from Kanto Chemical Co., Inc(>97%, Tokyo, Japan). *N*-Bromosuccinimide (NBS) and K_2CO_3 were purchased from Wako Pure Chemicals Industry Ltd (>97%, Osaka, Japan). These reagents were used as received. 1,4-Dioxane, chloroform, and *N*-dimethylformamide (DMF) were purchased from Kanto Chemical Co., Inc (>97%, Tokyo, Japan) were used after distillation.

Dibromides **1c-e** were prepared *via* the reaction of 1,3-dimethoxybenzene, 1,4-dimethoxybenzene, and 2,2'-dimethoxybiphenyl with NBS in $CHCl_3$ under reflux in 92, 94, and 98% yields, respectively. 2,2'-Dimethoxybiphenyl was prepared through the reaction of 2-biphenol with CH_3I in the presence of K_2CO_3 in acetone [4]. P_2O_5-MsOH mixture (w/w=1/10) was prepared according to Eaton's procedure [17].

2.2 Instruments

^{1}H NMR spectra were recorded on a JEOL ECX-400 (400 MHz) spectrometer (JEOL, Tokyo, Japan). Chemical shifts are expressed in parts per million (ppm) relative to the internal standard of Me_4Si (δ=0.00). ^{13}C NMR spectra were recorded on a JEOL ECX-400 (100 MHz) spectrometer (JEOL, Tokyo, Japan). Chemical shifts are expressed in parts per million (ppm) relative to the internal standard of $CDCl_3$ (δ=77.0). IR measurement was recorded on a JASCO FT/IR-4100 (JASCO, Tokyo, Japan). Mass spectra measurements were performed on a JEOL JMS-T100GCV High Performance Gas Chromatograph-Time-of-Flight Mass Spectrometer using FD ionization technique. Gel permeation chromatography (GPC) measurement was carried out at a flow rate of 1.0 mL min^{-1} at 40 ^{o}C using $CHCl_3$ as an eluent on a JASCO PU-2080 equipped with a UV detector (254 nm) and a Shodex K-804L column (Showa Denko, Tokyo, Japan). Glass transition temperatures (T_g) were estimated on the basis of DSC thermograms. The DSC thermograms (50-300 ^{o}C) were recorded on a Perkin Elmer DSC 4000 differential scanning calorimeter with a heating rate of 10 K min^{-1}. Thermal degradation temperatures (T_d) were estimated on the basis of TGA thermograms. The TGA thermograms(50-800 ^{o}C) were recorded on a Perkin Elmer TGA 4000 thermogravimeter with a heating rate of 10 K min^{-1}. UV-vis spectra were measured as a coating film on a ca.1.2 mm thin microscope slide on a JASCO V-630 spectrophotometer (JASCO, Tokyo, Japan).

2.3 Preparation of monomers ***3a-e***

To a 30 mL two-necked flask equipped with a reflux condenser and a N_2 balloon were added dibromoarene (**1a-e**, 1 mmol), *o*-methoxyphenylboronic acid (**2**, 455.9 mg, 3 mmol), $Pd(PPh_3)_4$ (231.2 mg, 0.2 mmol), K_2CO_3 (829.3 mg, 6 mmol), 1,4-dioxane (6 mL), and H_2O (3 mL). After the mixture was stirred at 90 ^{o}C for 8 h, it was poured into aqueous 2M HCl in a beaker. The separated aqueous layer was extracted with ethyl acetate three times. The combined extracts were dried over anhydrous $MgSO_4$. After removal of the drying agent, ethyl acetate was removed under reduced pressure. The residue was purified by column chromatography ($CHCl_3$) to afford the corresponding monomer **3a-e** in 58-97% yields.

Monomer **3a** [18]: Yield: 94%. ^{1}H NMR δ (400 MHz, $CDCl_3$): 3.81 (6H, s), 6.96-7.07 (4H, m), 7.31 (2H, t, J = 7.8 Hz), 7.36 (2H, d, J = 7.8 Hz), 7.43 (1H, t, J = 6.8 Hz), 7.49 (2H, d, J = 6.8 Hz), 7.67 (1H, s) ppm. ^{13}C NMR δ (100 MHz, $CDCl_3$): 55.7, 111.2, 120.9, 127.7, 128.3, 128.7, 130.7, 130.9, 131.2, 138.3, 156.6 ppm. IR υ(KBr): 1119, 1242, 1463, 1492, 1583, 1599 cm^{-1}.

Monomer **3b** [19]: Yield: 97%. ^{1}H NMR δ (400 MHz, $CDCl_3$): 3.47 (6H, s), 6.69 (2H, d, J = 7.8 Hz), 6.81 (2H, t, J = 7.8 Hz), 7.06 (2H, d, J = 7.8 Hz), 7.14 (2H, t, J = 7.8 Hz), 7.39 (4H, s) ppm. ^{13}C NMR δ (100 MHz, $CDCl_3$): 55.0, 110.2, 119.9, 127.2, 128.2, 130.6, 130.6, 131.0, 131.5, 156.3 ppm. IR υ(KBr): 1122, 1181, 1237, 1247, 1432, 1465, 1495 cm^{-1}.

Monomer **3c** [20]: Yield: 87%. ^{1}H NMR δ (400 MHz, $CDCl_3$): 3.79 (6H, s), 3.83 (6H, s), 6.64 (1H, s), 6.93-7.01 (4H, m), 7.17 (1H, s), 7.23-7.32 (4H, m) ppm. ^{13}C NMR δ (100 MHz,

$CDCl_3$): 55.8, 55.8, 95.9, 111.1, 119.5, 120.4, 127.6, 128.4, 132.0, 134.3, 157.2, 157.3 ppm. IR υ(KBr): 1202, 1241, 1319, 1458, 1480 cm^{-1}.

Monomer **3d** [20]: Yield: 58%. ^1H NMR δ (400 MHz, $CDCl_3$): 3.72 (6H, s), 3.89 (6H, s), 6.90 (2H, s), 6.98-7.06 (4H, m), 7.31-7.37 (4H, m) ppm. ^{13}C NMR δ (100 MHz, $CDCl_3$): 55.8, 56.6, 111.2, 115.3, 120.5, 127.4, 127.9, 128.8, 131.7, 150.9, 157.1 ppm. IR υ (KBr): 1119, 1248, 1433, 1488, 1513 cm^{-1}.

Monomer **3e**: Yield: 69%. ^1H NMR δ (400 MHz, $CDCl_3$): 3.81 (6H, s), 3.82 (6H, s), 6.93-7.06 (6H, m), 7.28 (2H, d, *J* = 7.3 Hz), 7.34 (2H, d, *J* = 7.3 Hz), 7.49-7.57 (4H, m) ppm. ^{13}C NMR δ (100 MHz, $CDCl_3$): 55.6, 55.8, 110.6, 111.1, 120.8, 127.3, 128.1, 129.8, 130.4, 130.5, 130.9, 133.0, 156.3, 156.5 ppm. IR υ (KBr): 1119, 1253, 1483, 1508 cm^{-1}. HRMS(FD) calcd for $C_{28}H_{26}O_4$ 426.1832. found 426.2665.

*2.4 Synthesis of aromatic polyketones **5a-e***

To a 30 mL one-necked flask equipped with a N_2 balloon were added dibromoarene **3a-e** (0.5 mmol), *trans*-1,4-cyclohexanedicarboxylic acid (**4**, 86.1 mg, 0.5 mmol), and P_2O_5-CH_3SO_3H mixture (1.5 mL). The mixture was stirred at 60 ^{o}C for 8 or 24 h(24 h for **5a-d**, 8 h for **5e**). After dilution with 7.5 mL of MsOH, the mixture was poured into MeOH in a beaker. The precipitate was collected by suction filtration to yield aromatic polyketone **5a-e** as white powders in 86-95% yields.

Polyketone **5a**: Yield: 86%. ^1H NMR δ (400 MHz, $CDCl_3$): 1.60-1.85(4H, m), 1.93-2.15 (4H, m), 3.21-3.48 (2H, m), 3.75-4.05 (6H, m), 6.96-7.12 (2H, m), 7.41-7.60 (3H, m), 7.63-7.74 (1H, m), 7.92-8.10 (4H, m) ppm. ^{13}C NMR δ (100 MHz, $CDCl_3$): 28.9, 44.6, 55.9, 110.7, 128.0, 128.7, 129.1, 129.8, 130.7, 131.5, 137.5, 160.5, 202.0 ppm. IR υ (KBr): 1672 cm^{-1}.

Polyketone **5b**: Yield: 92%. ^1H NMR δ (400 MHz, $CDCl_3$): 1.35-1.83 (8H, m), 2.95-3.11 (2H, m), 3.52-3.68 (6H, m), 6.72-6.83 (2H, m), 7.34-7.48 (2H, m), 7.61-7.68 (2H, m), 7.74-7.83 (2H, m) ppm. ^{13}C NMR δ (100 MHz, $CDCl_3$): 28.9, 44.4, 55.5, 110.3, 127.8, 128.3, 129.5, 130.5, 130.5, 132.0, 137.1, 160.2, 201.1 ppm. IR υ (KBr): 1672 cm^{-1}.

Polyketone **5c**: Yield: 86%. ^1H NMR δ (400 MHz, $CDCl_3$): 1.62-1.74 (4H, m), 1.96-2.12 (4H, m), 3.24-3.36 (2H, m), 3.76-3.98 (12H, m), 6.62-6.67 (1H, m), 6.96-7.04 (2H, m), 7.14-7.20 (1H, m), 7.90-8.02 (4H, m) ppm. ^{13}C NMR δ (100 MHz, $CDCl_3$): 28.9, 44.6, 55.9, 56.0, 95.7, 110.7, 118.4, 127.2, 128.6, 129.7, 132.8, 134.1, 157.6, 161.1, 202.2 ppm. IR υ (KBr): 1671 cm^{-1}.

Polyketone **5d**: Yield: 95%. ^1H NMR δ (400 MHz, $CDCl_3$): 1.62-1.74 (4H, m), 1.96-2.12 (4H, m), 3.24-3.36 (2H, m), 3.76-3.98 (12H, m), 6.62-6.67 (1H, m), 6.96-7.04 (2H, m), 7.14-7.20 (1H, m), 7.90-8.02 (4H, m) ppm. ^{13}C NMR δ (100 MHz, $CDCl_3$): 28.9, 44.7, 56.1, 56.6, 110.7, 114.9, 126.8, 127.7, 128.7, 130.1, 132.4, 150.8, 161.0, 202.1 ppm. IR υ (KBr): 1671 cm^{-1}.

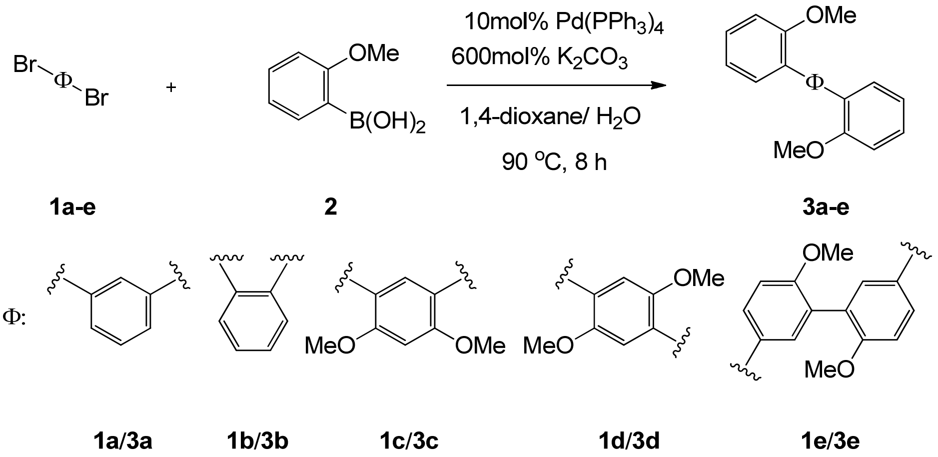
Polyketone **5e**: Yield: 87%. ^1H NMR δ (400 MHz, $CDCl_3$): 1.49-1.83 (4H, m), 1.85-2.19 (4H, m), 3.21-3.43 (2H, m), 3.71-4.05 (12H, m), 6.85-7.16 (4H, m), 7.38-7.65 (4H, m), 7.82-8.14 (4H, m) ppm. ^{13}C NMR δ (100 MHz, $CDCl_3$): 28.9, 44.6, 55.9, 55.9, 110.7, 110.8, 127.2, 129.1, 129.3, 129.4, 129.9, 130.5, 131.4, 132.9, 156.6, 160.5, 202.1 ppm. IR υ (KBr): 1671 cm^{-1}.

3. Results and Discussion

*3.1 Preparation of monomers **3a-e***

At first, 1,3-dibromobenzene (**1a**) was treated with 3 equimolar amounts of *o*-methoxyphenylboronic acid (**2**) in the presence of 10 mol% $Pd(PPh_3)_4$ and 6 equimolar amounts of K_2CO_3 in DMF at 110 ^{o}C for 8 h. However, the major product wasn't compound **3a** but monoarylated arene, due to insufficient reactivity. Next, the reaction was performed in a bilayer system using 1,4-dioxane/H_2O mixed solvents (v/v=2/1) at 90^{o}C for 8 h, affording compound **3a** as a single product in 87% yield. ^1H NMR spectrum of monomer **3a** is shown in Figure 2((a), in total)/((b), 6.7-8.2 ppm). The signals(overlapping of a doublet signal and a triplet one) are observed at 6.96-7.07 ppm, which are assignable to the *o*-

protons(d and f, indicated in Figure 2(b)) to OMe group. The signals derived from the central benzene ring are observed at 7.43(triplet, c), 7.49(doublet, b), and 7.67(singlet, a) ppm, respectively. Use of the bilayer system is effective because K_2CO_3 dissolves well in 1,4-dioxane/H_2O. Other monomers **3b**-**3e** were prepared in a similar manner in 58-97% yields. In the reactions of **1d** and **1e**, the yields decreased to 58 and 69%. ^{1}H NMR spectra of monomers **3b-e** are shown in Figure S1-4.



Scheme 1. Preparation of α,ω-bis(*o*-methoxyphenyl)arenes **3a-e**

Table 1. Preparation of α,ω-bis(*o*-methoxyphenyl)arenes **3a-e** via Suzuki-Miyaura coupling reaction[1].

1	3	Yield/%
1a	**3a**	94
1b	**3b**	97
1c	**3c**	87
1d	**3d**	58
1e	**3e**	69

[1] Reaction conditions: arene **1a-e** (1 mmol), *o*-methoxyphenylboronic acid (**2**, 3 mmol), K_2CO_3 (6 mmol), $Pd(PPh_3)_4$ (0.2 mmol), 1,4-dioxane (6 mL), H_2O (3 mL), 90°C, 8 h.

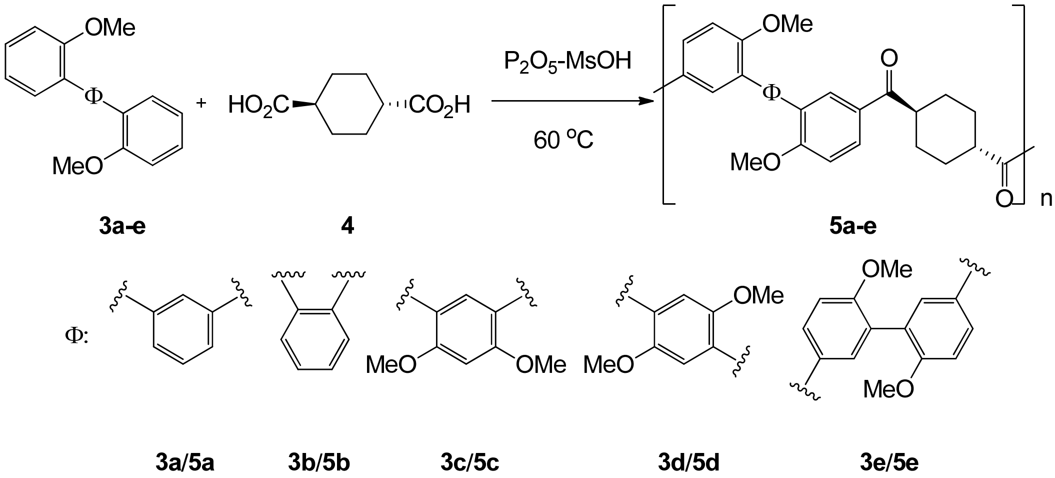
3.2 *Synthesis of aromatic polyketones* ***5a-e***

Monomers **3a-e** were treated with *trans*-1,4-cyclohexanedicarboxylic acid (**4**) in P_2O_5-CH_3SO_3H mixture (w/w=1/10) at 60 °C for 24 h, affording the corresponding cyclohexanediyl-bearing aromatic polyketones (**5a-e**)(Table 2). They were characterized by FT-IR, ^{1}H-NMR, and ^{13}C-NMR. IR spectra of polyketones **5a-e** have a strong peak at 1671-1672 cm^{-1}, which is assignable to an aromatic-alicyclic ketone C=O stretching vibration.

^{1}H NMR spectrum of polyketone **5a** is shown in Figure 2((c), in total)/((d), 6.7-8.2 ppm). The signals derived from cyclohexanediyl units are observed at 3.21-3.48 (2H, α-proton to C=O, h′ indicated in Figure 2(c)), 1.93-2.15 (4H, i′), and 1.60-1.85(4H, i′) ppm, respectively. The signal at 6.96-7.12 ppm is assignable to *o*-proton(2H, d′) to OMe group. The broad signal at 7.41-7.60 ppm is assignable to the protons(3H, b′ and c′) of 1,3-phenylene ring. Appearance of the broad signal at 7.92-8.10 ppm, which is assignable to o-protons(2H, e′ and g′) to C=O groups, indicates that diacylation proceeds at *p*-positions to the OMe group, regioselectively. ^{1}H NMR spectra of polyketones **5b-e** are shown in Figure S5-S8. In all spectra, the new broad signals above 7.8 ppm are observed like polyketone **5a**. In every ^{13}C NMR spectrum, the signal assignable to C=O carbon is observed at ~200 ppm. These observations also support that diacylation proceeds certainly. It should be noted that diacylation reaction always occurs at the *p*-positions to OMe groups of *o*-methoxyphenyl rings at both ends, regioselectively. Diacylation polymerization of monomers **3a** and **3b** occurs on more electron-rich aromatic rings at both ends than on the central benzene ring without OMe groups. In monomers **3c** and **3d**, the central benzene ring, which has two OMe groups, is more electron-rich than the aromatic rings at both ends, which has one OMe group. However, diacylation reaction occurs not on the central benzene ring but on the aromatic rings at both ends. Diacylation reaction at *p*-positions to OMe group, with less steric hindrance, occurs preferentially over at *o*/*m*-positions. It is supported by the fact that diacylation reaction of 2,2′-dimethoxybiphenyl occurs at 5,5′-positions, that is, at *p*-positions to OMe groups [4,6,16].

Incorporation of two *o*-methoxyphenyl groups at both ends makes monomers more active. GPC measurement disclosed molecular weights of polyketones **5a-e** are sufficiently high (M_w: 9600-35200) as shown in Table 2.

All of polyketones **5a-e** are highly soluble in typical organic solvents such as THF, $CHCl_3$, DMF, and NMP as shown in Table 3. Polyketones **5b-d** are more soluble than polyketones **5a** and **5e**. Incorporation of *o*-phenylene and dimethoxyphenoxy units as the central aromatic linkers improves the solubility of polyketones **5b-d**. Dihedral angles between the aromatic linker and *o*-methoxyphenyl group at both ends are larger, probably.



Scheme 2. Synthesis of aromatic polyketones **5a-e**

Table 2. P_2O_5-CH_3SO_3H-mediated synthesis of aromatic polyketones **5a-e**[1].

3	5	Time/h	Yield/ %	M_n [2]	M_w [2]	M_w/M_n [2]
3a	**5a**	24	86	6900	28200	4.1
3b	**5b**	24	92	8200	14200	1.7
3c	**5c**	24	86	13200	35200	2.7
3d	**5d**	24	95	7100	25400	3.6
3e	**5e**	8	87	6000	9600	1.6

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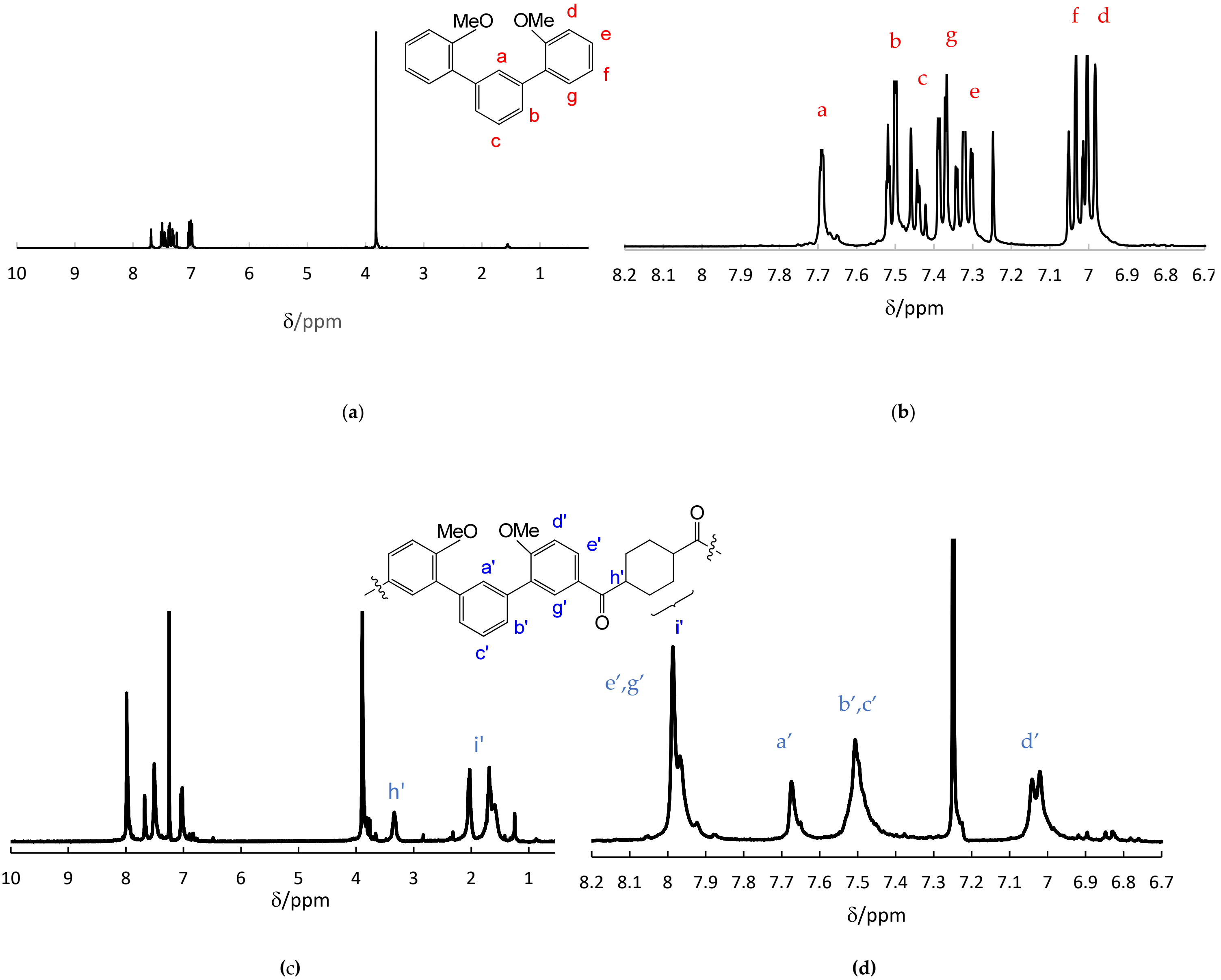
[1] Reaction conditions: arene **3a-e** (0.5 mmol), *trans*-1,4-cyclohexanedicarboxylic acid (**4**, 0.5 mmol), P_2O_5- CH_3SO_3H (1.5 mL), 60°C.[2] Estimated by GPC (eluent; $CHCl_3$) based on polystyrene standards.



(**a**) (**b**)

(c) (**d**)

Figure 2. H NMR spectra of monomer **3a**(**a**,**b**) and aromatic polyketone **5a**(**c**,**d**)

*3.3 Thermal properties of aromatic polyketones **5a-e***

Thermogravimetric analysis (TGA) in a nitrogen stream disclosed that polyketones **5a-e** have excellent thermal stability, No weight loss below ca. 400 °C is observed. There are no discriminative differences among thermal degradation of the five polyketones. Char yields at 800 °C are in the order to **5e**(48%)>**5d**(44%)>**5c**(32%)>**5a**(26%)>**5b**(20%). In most cases, the char yield increases with decreasing the ratio of the alicyclic(cyclohexanediyl) unit.

Glass transition temperatures (T_g) of polyketones **5a-e** were estimated by differential scanning calorimetry (DSC). The T_g value of the polyketone derived from 2,2′-dimethoxybiphenyl and 1,4-*trans*-cyclohexanedicarboxylic acid(**4**) [16] is 217 °C. Compared with this temperature, T_g values of the resulting polyketones (**5a-e**) are about the same or slightly lower. They are in the order to **5c**(219 ^{o}C)>**5e**(214 ^{o}C)>**5d**(205 ^{o}C)>**5a**(201 ^{o}C)>**5b**(188 ^{o}C). Introduction of more OMe groups increases T_g values to some extent due to their polarity(**5c**-**e** > **5a**,**b**).

Table 3. Solubility and thermal property of aromatic polyketones **5a-e**.

5	Solubility[1]					T_g/°C[2]	T_{d10}/°C[3]
	THF	$CHCl_3$	DMF	DMSO	NMP		
5a	++	++	++	+-	++	201	456
5b	++	+	++	+	++	188	447
5c	++	++	++	+	++	219	411
5d	++	++	++	+	++	205	428
5e	++	++	++	+-	++	214	442

[1] ++: soluble at room temperature. +: soluble on heating. +-: partially soluble. -: insoluble. [2] Determined on the basis of DSC curve. Heating rate: 10 K/min. [3] Temperature where a 10% weight was lost. Heating rate: 10 K/min.

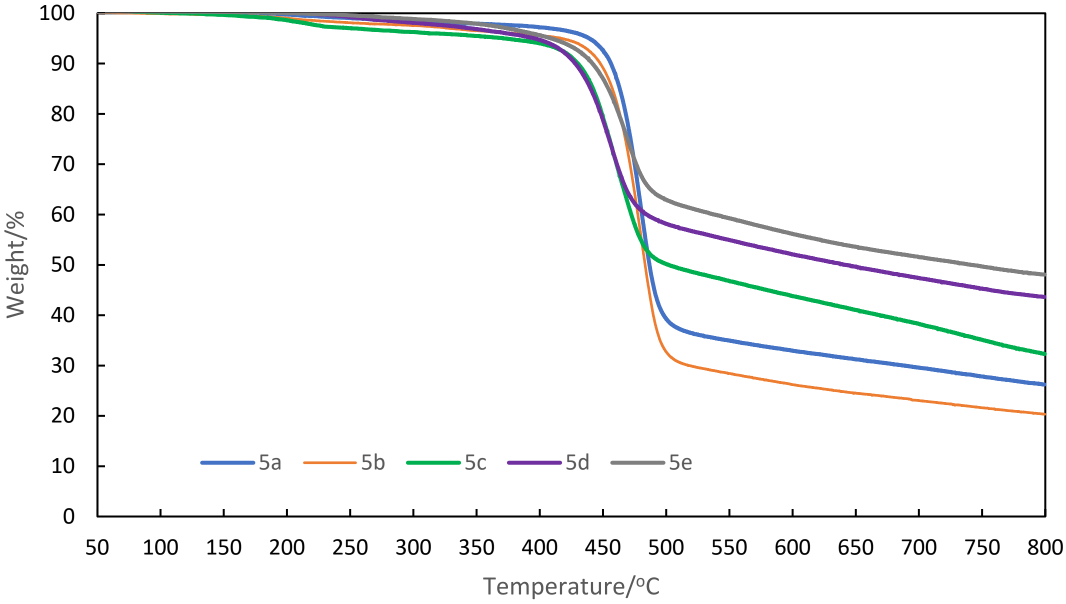


Figure 3. TGA thermograms of aromatic polyketones **5a-e**.

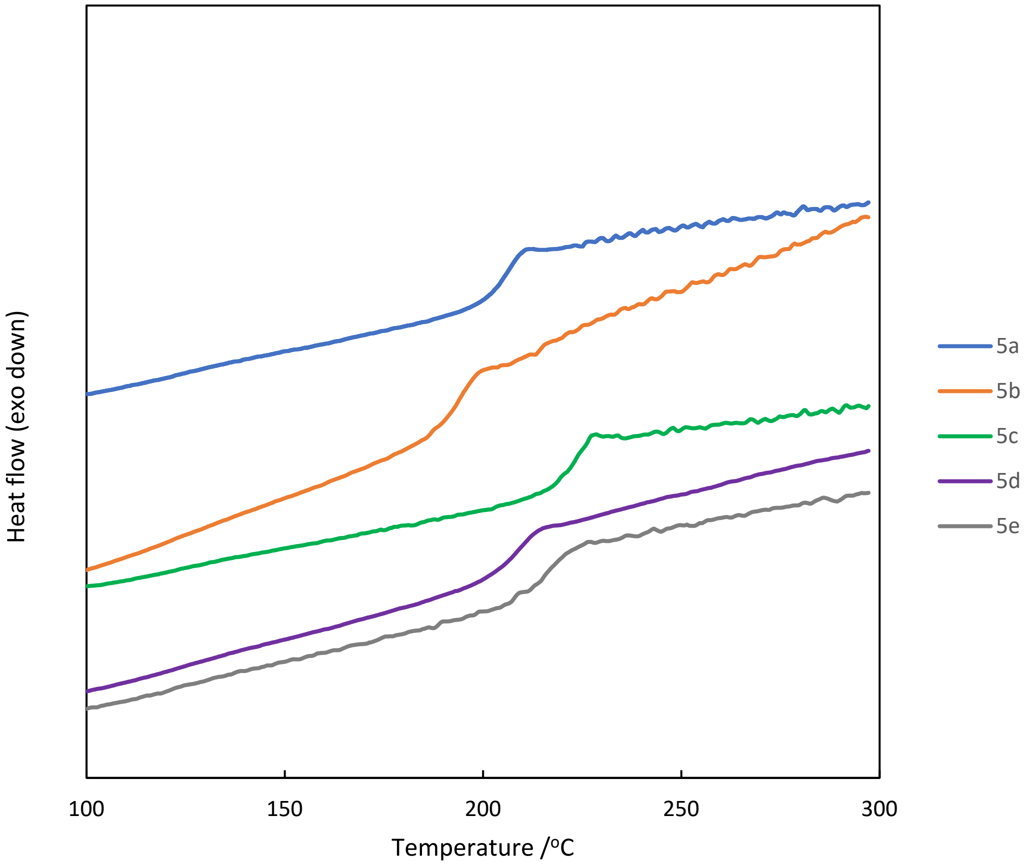


Figure 4. DSC thermograms of aromatic polyketones **5a-e**.

*3.4 Optical properties of aromatic polyketones **5a-e***

Figure 5 shows the UV-visible spectra of polyketone films **5a-e**(thickness: 3 µm), which were coated by solution casting from $CHCl_3$ solutions on a glass plate. Light transmittance values of films **3a-e** at 400 nm are 95%(**5a**), 90%(**5b**), 97%(**5c**), 84%(**5d**), and 94%(**5e**). Cutoff wavelengths range from 290 to 325 nm. All polyketones are sufficiently transparent as transparent materials. Probably, introduction of both alicyclic units and non-coplanar aromatic ones inhibits the interaction between polyketone chains suitably, which improves both organosolubility and transparency. In addition, introduction of alicyclic units inhibits formation of charge transfer complexes causing colorization to pale yellow.

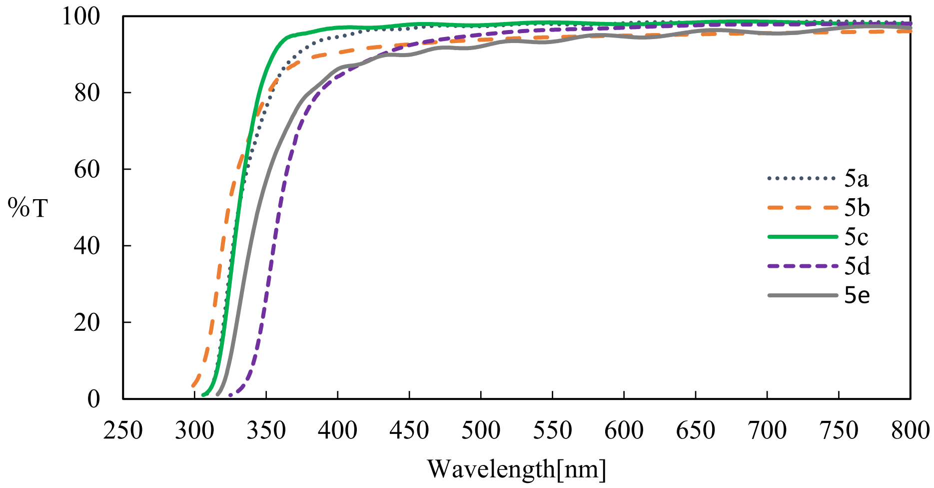


Figure 5.UV-vis spectra of aromatic polyketone films **5a-e**(thickness 3 μm).

4. Conclusions

A series of α,ω-bis(*o*-methoxyphenyl)arenes(**3a-e**) are prepared via palladium-catalyzed Suzuki-Miyaura coupling reaction of dibromoarenes with *o*-methoxyphenyl boronic acid. Aromatic polyketones bearing alicyclic units were synthesized through P_2O_5-MsOH-mediated direct condensation of α,ω-bis(*o*-methoxyphenyl)arenes(**3a-e**) with *trans*-1,4-cyclohexanedicarboxylic acid (**4**) proceeded effectively and regioselectively to afford aromatic polyketones bearing alicyclic units (**5a-e**). All of the resulting polyketones exhibit excellent thermal stability, solubility in organic solvents, and transparency. These materials will be applied to high-performance transparent materials such as displays, camera lens, and photolithography.

Supplementary Materials: The following supporting information can be downloaded at: http://www.mdpi.com, Scheme S1: ^{1}H NMR spectrum of monomer **3b**; Figure S2: ^{1}H NMR spectrum of monomer **3c**; Figure S3: ^{1}H NMR spectrum of monomer **3d**; Figure S4: ^{1}H NMR spectrum of monomer **3e**; Figure S5: ^{1}H NMR spectrum of polyketone **5b**; Figure S6: ^{1}H NMR spectrum of polyketone **5c**; Figure S7: ^{1}H NMR spectrum of polyketone **5d**; Figure S8: ^{1}H NMR spectrum of polyketone **5e.**

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