Electrophilic Aromatic Acylation Synthesis of Wholly Aromatic Polyketones Composed of 2,2′-Dimethoxybiphenylene Units

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ABSTRACT: Wholly aromatic polyketones have been successfully synthesized *via* AlCl₃-mediated Friedel–
Crafts acylation polymerization and P₂O₅-MsOH mediated direct condensation polymerization between 2,2′-
dimethoxybiphenyl (**1a**), an excellent acyl-acceptor monomer for electrophilic aromatic acylation polymerization, and
arenedicarboxylic acid derivatives.
    KEY WORDS   Aromatic Polyketones / Noncrystal Polymers / Friedel–Crafts Acylation / Wholly
        Aromatic Polyketones /

Aromatic polyketones have attracted much attention in respect of their excellent chemical and physical properties. While there are a lot of reports on aromatic polyketones,[1,2] almost all of them are classified as aromatic poly(*ether ketone*)s, *i.e.*, the aromatic polymers containing ether linkages together with ketonic carbonyl groups in the main chains. On the contrary, there are only a few reports on wholly aromatic polyketones, *i.e.* aromatic polyketones without ether linkages in the main chain.[3—7] Although nucleophilic aromatic substitution is the most effective chain elongation reaction for the syntheses of aromatic poly(ether ketone)s, it is inapplicable for the syntheses of wholly aromatic polyketones. In this course, the less effective methods, *i.e.*, electrophilic aromatic acylation such as Friedel–Crafts acylation and aromatic coupling reaction[8,9] are the residual choices of the protocol to wholly aromatic polyketones.

As one of the typical example of electrophilic aromatic acylation polymerization, Ueda and his coworkers have reported the efficient synthetic method for aromatic poly(ether ketone)s with the aid of phosphrous pentoxide-methanesulfonic acid mixture (P₂O₅-MsOH) as a condensing agent and solvent.[10—13] P₂O₅-MsOH mediated direct condensation is apparently preferable to AlCl₃-mediated polymerization when the producing polyketones have low solubility to organic solvents. We have also reported the synthesis of aromatic copoly(ether ketone)s having good adhesion property to steel surface.[14]

In the course of the study on the synthesis of aromatic polyketones, we have found that electrophilic aromatic substitution polymerization of 2,2′-dimethoxybiphenyl

(**1a**) and arenedicarboxylic acid derivatives readily gives wholly aromatic polyketones having appreciable molecular weights. In this paper, we would like to report that 2,2′-dimethoxybiphenyl (**1a**) is an excellent regioselective acyl-acceptor monomer having continuous reactivity and high regioselectivity in AlCl₃-mediated Friedel–Crafts-type polymerization and in P₂O₅-MsOH mediated direct condensation polymerization.[15]

EXPERIMENTAL

General

¹H NMR spectra were recorded on a JEOL GX-270 (270 MHz). Chemical shifts are expressed in ppm relative to internal standard of Me₄Si (δ, 0.00) or DMSO-d_6 (δ, 2.49). Inherent viscosities (η_{inh}) were determined by measurement of the flow time of polymer solution in concentrated H₂SO₄ (0.3 g dL⁻¹) at 30 °C using an Ostwald viscometer. The glass transition temperatures (T_g's) were determined on the basis of DSC curves. DSC curves were recorded on a SEIKO DSC-200 differential scanning calorimeter with a heating rate of 10 K min⁻¹ under nitrogen. Thermal degradation temperature (T_d) was determined on the basis of a TGA thermogram. The TGA thermogram was recorded on a SEIKO TG/DTA-200 thermogravimeter with a heating rate of 10 K min⁻¹.

2,2′-Dimethoxybiphenyl (**1a**) and 4,4′-dimethoxybiphenyl (**1b**) were prepared *via* dimethylation of the corresponding biphenols with Me₂SO₄. 2,2′-Dimethoxydiphenyl ether (**1c**) was prepared *via* Ullmann-type reaction of *o*-methoxyphenol (3 mmol),

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o-bromoanisole (2.5 mmol), potassium hydroxide (2.2 mmol), and cupper powder (5 mg) at 180°C for 2 h in a 38% yield. ^{1}H NMR (270 MHz) δ (CDCl$_3$): 3.85 (6 H, s), 6.77–7.13 (8 H, m) ppm. 2,2′-Bis(trifluoromethyl)biphenylene-4,4′-dicarboxylic acid (2d) was prepared according to our previous paper.[16–19] P$_2$O$_5$-MsOH was prepared according to Eaton's procedure.[20]

P$_2$O$_5$-MsOH Promoted Polymerization of 2,2′-Dimethoxybiphenyl (1a) and Dicarboxylic Acid 2

A solution of 2,2′-dimethoxybiphenyl (1a, 214 mg, 1.0 mmol) and dicarboxylic acid (2, 1.0 mmol) in P$_2$O$_5$-MsOH (3 g) was stirred for 24 h at 60°C. The reaction mixture was diluted with MsOH and the resulting solution was poured into saturated aqueous sodium carbonate to separate out a white solid. The solid was collected by suction filtration and dried *in vacuo* at 120°C to give polymer 3.

Polymer 3a: IR ν (KBr): 1651, 1593, 1241 cm^{-1}. ^{1}H NMR (270 MHz) δ (DMSO-d_6): 3.80 (6 H, s), 7.05–7.22 (6 H, m), 7.60–7.85 (8 H, m) ppm. Anal. Calc. for C$_{28}$H$_{20}$O$_5$: C, 77.06%; H, 4.59%. Found: C, 75.52%; H, 4.71%.

AlCl$_3$-Promoted Polymerization of 2,2′-Dimethoxybiphenyl (1a) and Dicarboxylic Acid Dichloride 5

To a solution of 2,2′-dimethoxybiphenyl (1a, 214 mg, 1.0 mmol) and dicarbonyl dichloride (5, 1.0 mmol) in 1,2-dichloroethane (4 mL), AlCl$_3$ was added by portions at 5°C under nitrogen atmosphere. The reaction mixture was stirred for 1 h at 5°C, warmed up to 15°C, and stirred further for 24 h at 15°C. The reaction was quenched by addition of methanol to separate out white precipitates. The precipitates were collected by suction filtration and dried *in vacuo* at 120°C to give a white solid of polymer 6. Polymer 6b: IR ν (KBr): 1655, 1595, 1257 cm^{-1}. ^{1}H NMR (270 MHz) δ (DMSO-d_6): 3.80–3.90 (6 H, m), 7.15–7.30 (2 H, m), 7.68–7.90 (8 H, m) ppm. Anal. Calc. for C$_{22}$H$_{16}$O$_4$: C, 76.74%; H, 4.65%. Found: C, 75.59%; H, 4.76%.

RESULTS AND DISCUSSION

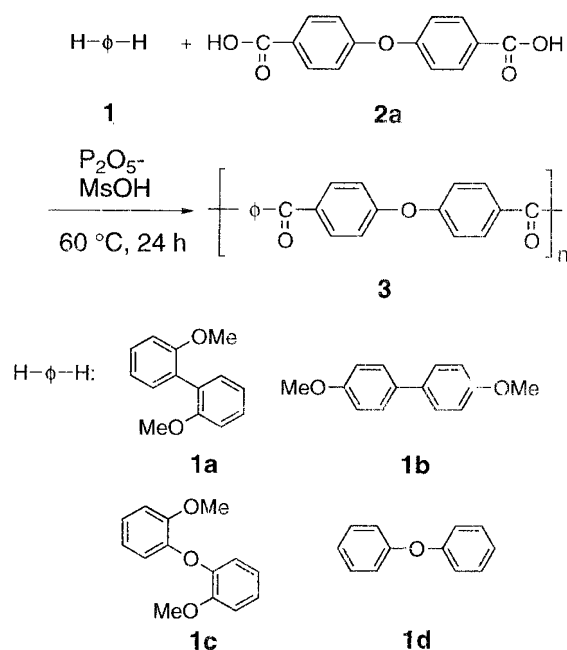*Reactivity of Several Acyl-acceptant Monomers*

As mentioned above, Ueda and his coworkers have reported P$_2$O$_5$-MsOH mediated electrophilic aromatic acylation polymerization of dicarboxylic acids containing phenyl ether structures such as 4,4′-oxybis(benzoic acid) (2a) with arenes to yield aromatic poly(ether ketone)s having high inherent viscosities.[10] They describe that phenyl ether structure in dicarboxylic acid is indispensable to regioselective acylation.[10]

According to this method, four kinds of electron-rich symmetrical arenes (1a–1d) were subjected to electrophilic aromatic acylation polymerization with 4,4′-oxybis(benzoic acid) (2a). The degree of polymerization was assessed on the basis of the inherent viscosity in a concentrated H$_2$SO$_4$ solution at 30°C. The results are summarized in Table I. When 2,2′-dimethoxybiphenyl (1a) was allowed to react with carboxylic acid 2a, the highest-molecular-weight poly(ether ketone) was obtained (η_{inh}, 0.49 dL g^{-1}). 2,2′-Dimethoxydiphenyl ether (1c) also shows effective reactivity for electrophilic aromatic acylation polymerization to give a poly(ether ketone) having moderate inherent viscosity. One of the common structural characteristics in the two effective acyl-acceptant monomers, 1a and 1c, is that two methoxy groups are situated at the o-positions. The two methoxy groups of monomer 1a not only activate the reactivity through electron-donating effect but also bring a twist in the biphenylene unit, which probably prevent the resulting

Table I. P$_2$O$_5$-MsOH mediated polymerization of arene 1 and 4,4′-oxybis(benzoic acid) (2a)[a]

Arene 1	Polymer 3	η_{inh}/dL g^{-1}[b]
1a	3a	0.49
1b	3b	0.14
1c	3c	0.34
1d	3d	0.12

[a]Reaction conditions, arene 1: 1 mmol, 4,4′-oxybis(benzoic acid) (2a): 1 mmol, P$_2$O$_5$-MsOH: 3 g, 60°C, 24 h. [b]Inherent viscosity was determined in a concentrated H$_2$SO$_4$ solution (0.3 g dL^{-1}) at 30°C.
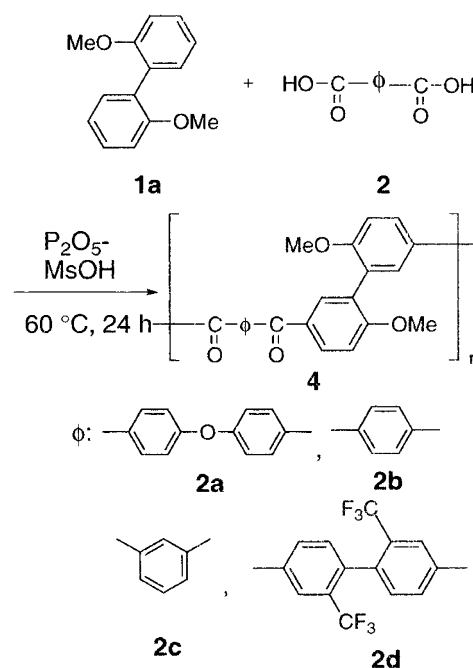

Scheme 1.

oligomer from aggregation and precipitation.

P₂O₅-MsOH Mediated Polymerization of 2,2′-Dimethoxybiphenyl (1a) with Several Arenedicarboxylic Acid Derivatives

2,2′-Dimethoxybiphenyl (**1a**), one of the most effective acyl-acceptor monomers for P₂O₅-MsOH mediated electrophilic aromatic acylation polymerization with 4,4′-oxybis(benzoic acid) (**2a**), also gives polyketones in the reaction with several arenedicarboxylic acids having no phenyl ether structures. When terephthalic acid (**2b**) or isophthalic acid (**2c**) was allowed to react with 2,2′-dimethoxybiphenyl (**1a**) in P₂O₅-MsOH, a polyketone with rather moderate molecular weight was obtained. The less reactivity in P₂O₅-MsOH mediated polymerization of 2,2′-dimethoxybiphenyl (**1a**) with terephthalic acid (**2b**) or isophthalic acid (**2c**) probably depends on insufficient activation of these carboxylic acids by P₂O₅-MsOH for sustainable acylation. On the other hand, biphenylenedicarboxylic acid bearing CF₃ groups (**2d**) gave a polymer having low inherent viscosity *via* P₂O₅-MsOH mediated direct polycondensation with biphenyl **1a**. The obtained polyketone is, however, estimated to have an appreciable molecular weight because in the ¹H NMR spectrum of the resulting polymers, the signal of the proton at the terminal unit is negligibly small against that of methoxy group. Accordingly, lower inherent viscosity of the resulting polyketone (**4d**) probably owes to weakness of intermolecular interaction between the polymer chains strongly polarized by CF₃ substituents.[16, 17, 21] The excellent reactivity in the P₂O₅-MsOH mediated polymerization of 2,2′-dimethoxybiphenyl (**1a**) with carboxylic acid **2d** depends on electron-deficiency of carboxy groups of dicarboxylic acid **2d** through strong electron-withdrawing effect of CF₃ group. Then, for realization of regioselective electrophilic aromatic acylation, milder activation such as transformation of the carboxy group into mixed acid anhydride type acylinium ion equivalent is preferable. Therefore, activation by P₂O₅-MsOH through the formation of mixed acid anhydride equivalent is more effective than that *via* Friedel–Crafts type activation by AlCl₃.

Friedel–Crafts-type Polymerization of 2,2′-Dimethoxybiphenyl (1a) with Dicarboxylic Acid Dichloride 5

AlCl₃-promoted Friedel–Crafts acylation polymerization of 2,2′-dimethoxybiphenyl (**1a**) and terephthaloyl chloride (**5b**) in 1,2-dichloroethane at 15°C afforded polymer **6b** with an inherent viscosity of 0.68 dL g⁻¹. When the reaction was performed at 30 °C, the inherent viscosity of the resulting polyke-

Scheme 2.

Table II. P₂O₅-MsOH mediated polymerization of 2,2′-dimethoxybiphenyl (**1a**) and dicarboxylic acid **2**[a]

Carboxylic acid **2**	Yield/%	η_{inh}/dL g⁻¹[b]
2a	99	0.49
2b	93	0.23
2c	78	0.23
2d[c]	>99	0.09

[a]Reaction conditions(except for **2d**), monomer **1a**: 1 mmol, monomer **2**: 1 mmol, P₂O₅-MsOH: 3 g, 60 °C, 24 h. [b]Inherent viscosity was determined in a concentrated H₂SO₄ solution (0.3 g dL⁻¹) at 30 °C. [c]Reaction conditions: 80 °C, 2 h.

tone was 0.15 dL g⁻¹. In addition, during the reaction at 30 °C, the reaction mixture was turned to deep red. As a matter of course, side reactions, *e.g.*, attack of aromatic rings to carbonyl carbon, probably occurs at the temperature higher than 30°C. Polymerization in other solvents such as CH₂Cl₂, CHCl₃, and PhNO₂ gave lower-molecular-weight polymer than that obtained in 1,2-dichloroethane.[22] On the other hand, isophthaloyl chloride (**5c**) and 2,6-naphthalenedicarbonyl chloride (**5d**) underwent the reaction with 2,2′-dimethoxybiphenyl (**1a**), affording polymers **6c** and **6d**, respectively, with inherent viscosities of 0.24 dL g⁻¹.

The results of the polymerization of 2,2′-dimethoxybiphenyl (**1a**) shown in Tables II and III reveal that monomer **1a** is also a suitable acyl-acceptor monomer for AlCl₃-promoted Friedel–Crafts acylation polymerization with conventional arenedicarboxylic acids with no arylene ether units, which is just the structural requisite for synthesis of wholly aromatic polyketones. The preference of AlCl₃-promoted

Table III. AlCl$_3$-mediated polymerization of 2,2′-dimethoxybiphenyl (**1a**) and dicarbonyl dichloride **5**[a]

Dicarbonyl dichloride **5**	Polymer **6**	Solvent	Yield/%	η_{inh}/dL g^{-1}[b]
5b	**6b**	ClCH$_2$CH$_2$Cl	99	0.68
		CH$_2$Cl$_2$	65	0.16
		CHCl$_3$	75	0.19
		PhNO$_2$	74	0.10
5c	**6c**	ClCH$_2$CH$_2$Cl	78	0.24
		CH$_2$Cl$_2$	66	0.17
		CHCl$_3$	71	0.13
		PhNO$_2$	77	0.27
5e	**6e**	ClCH$_2$CH$_2$Cl	78	0.24

[a]Reaction conditions, monomer **1a**: 1 mmol, monomer **5**: 1 mmol, AlCl$_3$: 2.7 mmol, Solvent: 4 mL, 20 °C, 24 h. [b]Inherent viscosity was determined in a concentrated H$_2$SO$_4$ solution (0.3 g dL^{-1}) at 30 °C.

Scheme 3.

Table IV. Glass transition temperatures of aromatic polyketones[a]

Monomers	Polymer	η_{inh}/dL g^{-1}[b]	T_g/°C[c]
1a+5b	**6b**	0.68	222
1a+5c	**6c**	0.24	200
1a+5e	**6e**	0.24	217
1a+2a	**3a**	0.49	200
1d+5b		0.45	172

[a]Reaction conditions, monomer **1**: 1 mmol, monomer **5**: 1 mmol, AlCl$_3$: 2.7 mmol, Solvent: 4 mL, 20 °C, 24 h. [b]Inherent viscosity was determined in a concentrated H$_2$SO$_4$ solution (0.3 g dL^{-1}) at 30 °C. [c]T_g was determined on the basis of DSC curves. Heating rate, 10 K min^{-1}.
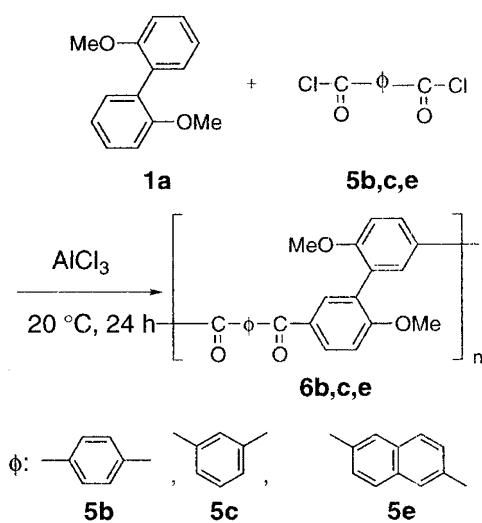
Friedel–Crafts acylation polymerization to P$_2$O$_5$-MsOH mediated direct condensation polymerization probably depends on higher activation of carboxylic acids or their derivatives. As already described, the sufficient reactivity of arenedicarboxylic acid containing CF$_3$ group (**2d**) in P$_2$O$_5$-MsOH mediated direct condensation polymerization is probably due to the electron-deficiency of the carbonyl groups of dicarboxylic acid itself.

Thermal Property of Polymer 6

On the basis of the DSC curves, T_g's of the resulting polyketones were determined. Wholly aromatic polyketones **6b**, **6c**, and **6e** show no melting points. The *p*-phenylenedicarbonyl skeleton of polymer **6b** is considered to have more rigid than the *m*-phenylenedicarbonyl skeleton of polymer **6c**. The different rigidities of the polyketones probably affect their T_g's: 220 °C for polymer **6b** and 200 °C for polymer **6c**. In addition, T_g of the poly(ether ketone) obtained in the reaction of diphenyl ether and terephthaloyl chloride is 172 °C and that of poly(ether ether ketone) (PEEK) is 143 °C. These values show that there is a tendency that decrease in the portion of ether linkage in the main chain increases T_g. This tendency is accountable as follows: removal of flexible ether bond where free rotation occurs, improves thermal resistibility of the polyketone.

Thermal degradation temperature (T_d) of polymer **6b** was determined on the basis on TGA thermograms recorded under nitrogen. The 5% weight loss of polymer **6b** occurs at 418 °C. The thermal resistibility is almost the same as poly(ethylene terephthalate). The existence of methoxy group presumably incurs oxidation of methoxyarene moiety or thermal scission of the main chain.[23]

Copolymerization

Two types of copolymerization about acyl-acceptant monomer **1a** were undertaken to clarify the relationship between molecular structure and T_g. One is the copolymerization of the combination of acyl-acceptant monomers **1a** and **1d** with terephthaloyl chloride (**5b**). The other is the copolymerization of acyl-acceptant monomer **1a** with the combination of arenedicarboxylic acids **5b** and **5e**.

Table V. AlCl$_3$-mediated copolymerization of arene **1** and dicarbonyl chloride **5**[a]

Monomer/mmol				η_{inh}/dL g^{-1}[b]	T_g / °C[c]
1a	**1d**	**5b**	**5e**		
1	0	1		0.68	222
0.8	0.2	1		0.24	220
0.5	0.5	1		0.35	204
0.2	0.8	1		0.49	191
0	1	1		0.45	172
1		0.8	0.2	0.53	223
1		0.5	0.5	0.38	224
1		0.2	0.8	0.36	227
1		0	1	0.24	217

[a]Reaction conditions, AlCl$_3$: 2.7 mmol, Solvent: 4 mL, 20 °C, 24 h. [b]Inherent viscosity was determined in a concentrated H$_2$SO$_4$ solution (0.3 g dL^{-1}) at 30 °C. [c]T_g was determined on the basis of DSC curves. Heating rate, 10 K min^{-1}.

The results of copolymerization of 2,2′-dimethoxybiphenyl (**1a**) and diphenyl ether (**1d**) with terephthaloyl chloride (**5b**) are shown in Table V. Increase in the portion of 2,2′-dimethoxybiphenylene unit gradually increases T_g of the copolymer. This is reasonably interpreted to be caused by the higher rigidity of 2,2′-dimethoxy-5,5′-biphenylene than 4,4′-oxybiphenylene unit having ether bond.

The results of the copolymerization of terephthaloyl chloride (**5b**) and 2,6-naphthalenedicarbonyl chloride (**5e**) with 2,2′-dimethoxybiphenyl (**1a**) are also shown in Table V. These results imply that the T_g of the resulting copolymer decreases with increasing in the portion of 2,6-naphthalenedicarbonyl unit, which decreases the degree of polymerization at the same time. This behavior presumably owes to the lower solubility of the resulting polyketone in 1,2-dichloroethane.

CONCLUSIONS

We have succeeded in the synthesis of wholly aromatic polyketones using 2,2′-dimethoxybiphenyl (**1a**) as the acyl-acceptor monomer. For the synthesis of wholly aromatic polyketones bearing 2,2′-dimethoxy-5,5′-biphenylene units except for those bearing CF$_3$ groups, AlCl$_3$-mediated Friedel–Crafts acylation is the superior method to P$_2$O$_5$-MsOH mediated direct polycondensation. The resulting wholly aromatic polyketones have higher T_g values than poly(ether ketone)s.

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