P₂O₅-MsOH-mediated Facile Synthesis of Semi-aromatic Polyketones Bearing 1,4-Cyclohexanediyl Units

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Direct polycondensation of *trans*-1,4-cyclohexanedicarboxylic acid with several electron-rich arenes in a P_2O_5 -CH₃SO₃H (MsOH) mixture gave semi-aromatic polyketones bearing 1,4-cyclohexanediyl units in the main chains. The resulting polyketones have sufficiently high thermal stability and excellent transparency.

Aromatic polyketones have received much attention from the viewpoint of their excellent chemical and physical stability, high mechanical strength, and biocompatibility.^{1,2} In general, almost all aromatic polyketones, including poly(ether ether ketone) (PEEK), have pale yellow or brown color. If colorless and transparent aromatic polyketones had been developed, they would have been applied in high-performance optical materials such as transparent films and camera lenses. One of the effective approaches is the replacement of part of the aromatic units with alicyclic ones, and various semi-aromatic polymers have been developed thusly.³ Turner et al. reported aromatic poly(ether sulfone)s and poly(ether ether ketone)s bearing 1,4-cyclohexanediyl units using 1,4-cyclohexanedicarboxylic acid as the starting material.^{4a} We also reported the synthesis of aromatic poly(ether ketone)s bearing alicyclic units in the main chains through nucleophilic aromatic substitution polymerization between bisphenols and bis(fluorobenzoyl)cycloalkanes.^{4b} The resulting polyketones have relative transparency against typical aromatic polyketones.^{1,2} There is, however, ample room for further improvement of transparency. This motivated us to synthesize highly transparent semi-aromatic polyketones through another polymerization method, i.e., electrophilic aromatic substitution polymerization.

In this letter, we report the *facile* synthesis of transparent semi-aromatic polyketones through P_2O_5 -MsOH⁵-mediated direct polycondensation between electron-rich arenes **1a–1e** and *trans-*1,4-cyclohexanedicarboxylic acid (**2**),⁶ which is one of the simple and commercially available alicyclic dicarboxylic acids (Scheme 1).

2,2'-Dimethoxybiphenyl $(1a)^{2a}$ was allowed to react with *trans*-1,4-cyclohexanedicarboxylic acid (2) in a P₂O₅-MsOH mixture as a mediator and a solvent at 60 °C for 24 h. As the reaction proceeded, the reaction mixture turned highly viscous. The viscous reaction mixture was poured into methanol for work up. The resulting polymer **3a** was clearly a white powder, but was insoluble in CHCl₃. To improve the solubility of the polyketone, 2,2'-alkoxybiphenyls with long alkyl chains **1b** and **1c** were employed. The resulting polyketones **3b** and **3c** were white powders that dissolved completely in CHCl₃. As other electron-rich acyl-acceptant monomers, diphenyl ether $(1d)^{2a}$ and 2,2'-dimethoxydiphenyl ether $(1e)^{2a}$ were also employed,



Scheme 1. P_2O_5 -MsOH-mediated direct polycondensation of electron-rich arenes **1a**-1e with *trans*-1,4-cyclohexanedicarbox-ylic acid (2).

affording the corresponding aromatic polyketones 3d and 3e. IR measurements of polyketones 3a-3e disclosed a peak at 1671- 1672 cm^{-1} , which is assignable to the ketonic C=O stretching vibration. Structural identification, that is regioselectivity, was confirmed by ¹HNMR spectral measurements of the model compounds of monomers 1a, 1d, and 1e with cyclohexanecarboxylic acid (See Supporting Information, 5a, 5d, and 5e). As for 1a, the reaction proceeded at the 5,5'-positions regioselectively, due to the strong electron-donating effect of methoxy groups. As for 1d, the reaction proceeded regioselectively at the *p*-positions, due to the electron-donating effect of the ether unit. No reaction at the o-positions relative to the ether unit proceeded. As for 1e, the reaction proceeded at the 5,5'positions, i.e., the *p*-positions relative to the methoxy groups because methoxy groups are more electron-donating than aryloxy ones. On the other hand, 1,4-dimethoxybenzene or 1,3-dimethoxybenzene, which is activated by two methoxy groups, was inapplicable to these polymerizations. In fact, 1,3dimethoxybenzene reacted with 2 equimolar amounts of cyclohexanecarboxylic acid in P2O5-MsOH to form only a monoacylated product (See Supporting Information, 6f). After the first acylation of 1,3-dimethoxybenzene proceeded, the electron density of the monoacylated arene decreased, which would prevent further acylation of the monoacylated product. In contrast, 2,2'-dimethoxybiphenyl (1a) reacted with 2 equimolar amounts of cyclohexanecarboxylic acid in P2O5-MsOH to form the diacylated product along with trace amounts of the monoacylated product. Although the electron density of the directly acylated benzene ring of the monoacylated arene decreases, the electron density of the other benzene ring does not decrease so much due to the twisting structure between two benzene rings, i.e., less overlapping between two benzene rings, which maintains both the reactivity and regioselectivity at the 5'-position of the other benzene ring.^{2a} As for 1d and 1e, the

Table 1. Synthesis of aromatic polyketones 3a-3e^a

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3	Yield/%	$M_{\rm n}^{\rm b}$	$M_{ m w}{}^{ m b}$	$M_{\rm w}/M_{\rm n}^{\rm b}$
3a	90	c	c	c
3b	84	6100	26100	4.28
3c	91	6600	29000	4.39
3d	97	c	c	c
3e	98	35500	45300	1.28

^aReaction conditions: monomer **1a–1e** and **2** (0.5 mmol, respectively), P_2O_5 –CH₃SO₃H mixture (1.5 mL), 60 °C, 24 h. ^bEstimated by GPC (eluent; CHCl₃) based on polystyrene standards. ^cNot measured (insoluble in CHCl₃).

Table 2. Solubility and thermal properties of aromatic polyketones $\mathbf{3}^a$

3	THF	CHCl ₃	DMF	DMSO	NMP	$T_{\rm g}/^{\rm o}{\rm C}^{\rm b}$	$T_{\rm d10}/^{\circ}\rm C^{c}$
3a	_	_	+-	+-	+-	217	447
3b	+-	++	+-	+-	++	160	451
3c	+-	++	+-	+-	+-	95	439
3d	_	_	+-	+-	+-	d	460
3e	+	++	++	+	++	169	447

^a(++): soluble at rt; (+): soluble on heating; (+-): partially soluble; (-) insoluble. ^bDetermined on the basis of DSC curves. Heating rate: 10 Kmin^{-1} . ^cTemperature where a 10% weight loss occurs. Heating rate: 10 Kmin^{-1} . ^dNot observed below $300 \,^{\circ}\text{C}$.

existence of the aryl–O–aryl ether unit would maintain the reactivity of the second acylation reaction.

Table 1 summarizes the yields and the molecular weights of the resulting polyketones **3**. Polyketones **3b**, **3c**, and **3e**, which are soluble in CHCl₃, have such high molecular weights as to fabricate flexible thin films. In particular, the molecular weights of polyketone **3e** were much higher than those of polyketones **3b** and **3c**. The reason is that the electron density of **1e** is the highest among the screened ones due to electronic activation by both methoxy groups and one Ar–O–Ar ether unit. When regioisomeric *trans*-1,2-cyclohexanedicarboxylic acid was employed instead of *trans*-1,4-cyclohexanedicarboxylic acid (**2**), no polymerization proceeded. Probably, the reaction intermediate, i.e., mixed diacid dianhydride, would be destabilized due to steric hindrance from the two neighboring mixed acid anhydride units.

Table 2 shows the solubility of polyketones 3a-3e. Polyketones 3b, 3c, and 3e are soluble in typical solvents such as CHCl₃ and NMP. On the other hand, polyketone 3a and 3d are insoluble. As for 3b and 3c, the twisting structure between two benzene rings of 2,2'-dialkoxybiphenyls and suitable side alkyl chains will afford sufficient solubility. As for 3d, neither side alkyl chains nor the twisting of the main chains will decrease the solubility. As for 3e, two methoxy groups will not only activate the reactivity but also induce the twisting of the main chains, which will lead to high solubility.

Thermogravimetric analysis disclosed that the polyketones **3** have excellent thermal stability. No loss of weight with temperature, which ranged up to ca. 440 °C under N₂ flow, was observed. These thermal behaviors are similar to those of polyketones synthesized via nucleophilic aromatic substitution polymerization.^{4b} DSC measurements disclosed that polyketones



Figure 1. UV-vis spectra of aromatic polyketones 3b, 3c, and 3e.

3 have an amorphous nature. The glass-transition temperatures of polyketones 3 range from 95 to 217 °C. Probably, the introduction of long alkyl units affects the increase in organo-solubility and the decrease in $T_{\rm g}$ values.

Figure 1 shows the UV-visible spectra of polyketone films 3b, 3c, and 3e, which were coated by solution casting from CHCl₃ solutions on a glass plate. The transmittance of **3b** and **3c** in the visible light region is more than 96%, while that of 3e is more than 93% (3 µm thick). The cutoff wavelengths are 299 (3b), 305 (3c), and 320 nm (3e), respectively. Three polyketones are more transparent than the polyketones we reported previously.4b Switching the polymerization method from nucleophilic aromatic substitution polymerization in amide solvents at high temperature to electrophilic acylation polymerization in P₂O₅-MsOH at 60 °C improved the transparency of the polyketone films. Because the former polymerization needs to be performed under high temperature above 170 °C under basic conditions, side reactions such as thermal degradation of solvents and polyketones will occur. Furthermore, the increase in reaction temperature colors the polyketones more deeply. On the other hand, the P₂O₅-MsOH-mediated reaction can be performed at lower temperature (60 °C), which would suppress the side reactions causing color development.

In conclusion, semi-aromatic polyketones with 1,4-cyclohexanediyl units were obtained through P_2O_5 -MsOH-mediated direct polycondensation between electron-rich arenes with 1,4cyclohexanedicarboxylic acid (2). The resulting polyketones **3** have excellent thermal stability, organosolubility (except **3a** and **3d**), and transparency.

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Supporting Information is available electronically on J-STAGE.

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