Electronic Supplementary Information (ESI) for:

Nonstoichiometric Polycondensation based on Friedel-Crafts acylation in Superacid for the Synthesis of Aromatic Polyketones

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Materials and Methods

Materials

4,4’-Dicarboxydiphenyl ether (1) and 2,2’-dihydroxybiphenyl were purchased from Tokyo Chemical Industry Co., Ltd. and used as received. 2,2’-Dimethoxybiphenyl (2) was prepared by dimethylation of 2,2’-dihydroxybiphenyl using iodomethane and K₂CO₃ and used after recrystallization from acetonitrile. Trifluoromethanesulfonic acid (TFMSA), benzoic acid (3), benzyol chloride, AlCl₃, and 1,2-dibromoethane were purchased from Wako Pure Chemical Industries Ltd. and used as received.

Synthesis of monoacylated compound 4

To a solution of 2 (0.86 g, 4.0 mmol) and benzyol chloride (0.28 g, 2.0 mmol) in
dichloromethane (16 mL) was added AlCl$_3$ (0.53 mmol, 4.0 mmol) with stirring in an ice bath. After stirring for 4 h in the bath, the mixture was diluted with dichloromethane and washed with water. The solvent was removed by evaporation and the residue was purified by silica gel column chromatography (chloroform/hexane = 4/1, v/v) to give 4. The yield was 0.59 g (92%).

$^1$H NMR (DMSO-$_d_6$, $\delta$, ppm): 3.74 (s, 3H), 3.83 (s, 3H), 6.99 (t, 1H), 7.09 (d, 1H), 7.21 (d, 1H), 7.24 (d, 1H), 7.35 (t, 1H), 7.53-7.59 (overlapped, 3 H), 7.64 (t, 1H), 7.74 (d, 2H), 7.81 (d, 1H). $^{13}$C NMR (DMSO-$_d_6$, $\delta$, ppm): 55.42, 55.86, 111.13, 111.41, 120.16, 126.08, 127.11, 128.41, 128.69, 129.06, 129.26, 130.96, 131.47, 132.05, 133.16, 137.73, 156.59, 160.53, 194.32. Anal. Calcd for (C$_{21}$H$_{18}$O$_3$): C, 79.23; H, 5.70; Found: C, 79.15; H, 5.81.

**Synthesis of diacylated compound 5**

To a solution of 2 (0.32 g, 1.5 mmol) in TFMSA (2 mL) was added 3 (0.55 g, 4.5 mmol), and the resulting mixture was stirred at room temperature for 5 h. Then, the mixture was poured into water and the resulting precipitate was collected by filtration and washed with 5% NaHCO$_3$ aq. The resulting solid was purified by silica gel column chromatography (chloroform) to give 5. The yield was 0.59 g (93%). $^1$H NMR (DMSO-$_d_6$, $\delta$, ppm): 3.86 (s, 6H), 7.28 (d, 2H), 7.56 (t, 4H), 7.63-7.68 (overlapped, 4H), 7.73 (d, 4H), 7.82 (d, 2H). $^{13}$C NMR (DMSO-$_d_6$, $\delta$, ppm): 55.99, 111.30, 125.72, 128.41, 128.82, 129.29, 131.89, 132.13, 133.13, 137.62, 160.32, 194.25. Anal. Calcd for (C$_{28}$H$_{22}$O$_4$): C, 79.60; H, 5.25; Found: C, 79.53; H, 5.26.

**Synthesis of conformationally fixed compound 6**

A solution of 2,2'-dihydroxybiphenyl (0.50 g, 2.7 mmol), 1,2-dibromoethane (0.51 g, 2.7 mmol), and K$_2$CO$_3$ (1.69 g, 11 mmol) in acetone (150 mL) was refluxed for 12 h. The reaction mixture was concentrated by evaporation and poured into 0.1 M HCl aq. The resulting precipitate was collected by filtration, washed with water, and purified by silica gel column
chromatography (chloroform/hexane = 2/1, v/v) to give 6. The yield was 0.31 g (55%). $^1$H NMR (DMSO-$d_6$, $\delta$, ppm): 3.95 (d, 2H), 4.40 (d, 2H), 7.17 (d, 2H), 7.22 (t, 2H), 7.33 (d, 2H), 7.39 (t, 2H). $^{13}$C NMR (DMSO-$d_6$, $\delta$, ppm): 72.61, 122.43, 124.29, 129.64, 129.96, 131.52, 157.85. Anal. Calcd for (C$_{14}$H$_{12}$O$_2$): C, 79.23; H, 5.70; Found: C, 79.18; H, 5.75.

**Synthesis of monoacylated compound 7**

To a solution of 6 (0.21 g, 1.0 mmol) and benzoyl chloride (0.56 g, 4.0 mmol) in dichloromethane (10 mL) was added AlCl$_3$ (0.80 mmol, 6.0 mmol) with stirring in an ice bath. After stirring at room temperature for 12 h, the mixture was diluted with dichloromethane and washed with water. The solvent was removed by evaporation and the residue was purified by silica gel column chromatography (chloroform/hexane = 4/1, v/v) to afford 7. The yield was 0.19 g (59%). $^1$H NMR (DMSO-$d_6$, $\delta$, ppm): 4.02 (d, 2H), 4.51 (d, 2H), 7.21 (d, 1H), 7.25 (t, 1H), 7.33 (d, 1H), 7.42-7.47 (overlapped, 2H), 7.57 (t, 2H), 7.65-7.70 (overlapped, 2H), 7.76-7.82 (overlapped, 3H). $^{13}$C NMR (DMSO-$d_6$, $\delta$, ppm): 71.43, 72.28, 122.46, 122.59, 124.77, 128.53, 129.46, 129.74, 130.08, 130.30, 131.35, 131.44, 132.45, 132.53, 132.57, 137.20, 157.01, 161.30, 194.46. Anal. Calcd for (C$_{21}$H$_{16}$O$_3$): C, 79.73; H, 5.10; Found: C, 79.51; H, 5.31.

**General procedure of nonstoichiometric polycondensation**

A solution of 1 (0.078 g, 0.30 mmol) and 2 (0.077 g, 0.36 mmol) in TFMSA (0.45 mL) was stirred at 40 °C for 24 h. The mixture was poured into water and the resulting precipitate was collected by filtration and then dried in vacuo at room temperature for 3 h. The resulting polymer was dissolved in DMAc, reprecipitated into 2-propanol, and collected by filtration, followed by drying in vacuo at 80 °C for 12 h. The yield was 0.13 g (98%).
Model reactions

A solution of 2 (0.054 g, 0.25 mmol) or 6 (0.053 g, 0.25 mmol) and 3 (0.031 g, 0.25 mmol) in TFMSA (0.5 mL) was stirred at room temperature for 6 h. The resulting mixtures (10 µL) were directly diluted by DMSO-\textsubscript{d}\textsubscript{6} (680 µL) to carry out NMR measurements.

Model reaction for kinetics study

A solution of 2 (0.032 g, 0.15 mmol) and 3 (0.031 g, 0.25 mmol) in TFMSA (0.5 mL) was stirred at room temperature. The reaction was sampled (10 µL), diluted by DMSO-\textsubscript{d}\textsubscript{6} (680 µL), and monitored by NMR spectroscopy at various time points.

The kinetics of the model reaction was studied based on the following equations:

\[ 2 + 3 \xrightarrow{k_1} 4 \]
\[ 4 + 3 \xrightarrow{k_2} 5 \]

where 4 is an intermediate. Moreover,

\[ -\frac{d[3]}{dt} = k_1[2][3] + k_2[4][3], \quad (1) \]
\[ -\frac{d[2]}{dt} = k_1[2][3], \quad (2) \]
\[ \frac{d[4]}{dt} = k_1[2][3] - k_2[4][3], \quad (3) \]

and

\[ \frac{d[5]}{dt} = k_2[4][3]; \quad (4) \]

if \( k_2 \gg k_1 \), the amount of the intermediate 4 can be ignored in the steady state. Thus,

\[ \frac{d[4]}{dt} = 0. \quad (5) \]

From the equations (3) and (5), the concentration of 4 can be expressed as follows:

\[ [4] = \frac{k_1}{k_2}[2]. \quad (6) \]

The equation (4) can be expressed using the equation (6) as

\[ \frac{d[5]}{dt} = k_1[2][3]. \quad (7) \]
The concentrations of 2 and 3 are given by

\[ [2] = [2]_0 - [5] \text{ and } [3] = [3]_0 - 2[5]. \]

Therefore, the equation (7) is written as

\[ \frac{d[5]}{dt} = k_1 ([2]_0 - [5])([3]_0 - 2[5]). \]

This expression can be integrated under the condition that \([5] = 0\) at reaction time \(t = 0\) as follows:

\[ \ln \left( \frac{[2]}{[3]} \right) = (2[2]_0 - [3]_0)k_1 t + \ln \left( \frac{[2]_0}{[3]_0} \right). \]

**Preparation of films for tensile tests**

The polymer synthesized in the condition of \([2]_0/[1]_0 = 1.1 \) (\(M_w = 58,400, M_w/M_n = 1.7\)) was dissolved in DMAc (0.1 g/mL). The solution was cast onto a flat glass plate and heated at 60 °C for 30 min and at 100 °C for 30 min. Then the resulting film was dried under vacuum at 120 °C for 12 h. After peeling off from the glass plate, the film was cut into rectangular test pieces (\(W \times H = 5 \times 40 \text{ mm}\)) with about 50 \(\mu\text{m}\) thickness.

**Calculation methods**

The structures and \(^{13}\text{C}\) NMR chemical shifts of the compounds were calculated using the Gaussian 09 package.\(^{1}\) The structures of the compounds were optimized by density functional theory (DFT)-B3LYP/6-31G** level of calculations before NMR calculations. The \(^{13}\text{C}\) NMR chemical shifts were calculated by DFT-gauge including atomic orbital (GIAO) methods at the B3LYP level with the 6-31G** basis sets and referenced to \(\text{CH}_4\) (calculated absolute shift, i.e., \(\sigma(C) = 199.1\)).\(^{2}\)

**Measurements**
$^1$H and $^{13}$C NMR spectra were recorded using a JEOL JNM-ECX 500 NMR spectrometer (Jeol Co., Tokyo, Japan). GPC measurements were carried out using a Shodex RI-71S RI detector (Showa Denko K. K., Tokyo, Japan) and two Shodex LF804 polystyrene–divinylbenzene columns (Showa Denko K. K., Tokyo, Japan) with chloroform as the eluent. Differential scanning calorimetry (DSC) measurements were carried out using a DSC7000X (Hitachi High-Tech Science Co., Tokyo, Japan). The heating rate was set at 10 °C min$^{-1}$. Thermogravimetric analysis (TGA) measurements were carried out using a STA7300 (Hitachi High-Tech Science Co., Tokyo, Japan) at a heating rate of 10 °C min$^{-1}$. TGA and DSC measurements were performed using the polymer with $M_w$ of 58,400 and $M_w/M_n$ of 1.7. Tensile tests were performed using an EZ Test EZ-LX 50N tensile tester (Shimadzu Co., Kyoto, Japan) with a crosshead speed of 10 mm min$^{-1}$.

**Supplementary Characterization and Results**

**Calculation of $^{13}$C NMR shifts**

The $^{13}$C NMR chemical shifts of 4b and 4c were calculated by DFT-DIAO methods at the B3LYP level with the 6-31G**. The compound 4c is a methoxy-protonated and carbonyl-unprotonated form of 4b as shown in Table S1. The structures of 4b and 4c were optimized by DFT-B3LYP/6-31G** level of calculations before NMR calculations. The calculation result is shown in Table S1. The resulting calculated chemical shifts clearly show that the carbon signal of the reaction site in 4c (C$_3$ in 4c) appears at lower magnetic field compared with that in 4b (C$_3$ in 4b). Furthermore, the measured chemical shift of C$_3$ in 4b (in TFMSA) corresponds to the calculated chemical shift of C$_3$ in 4b. This result clearly indicates that the methoxy groups in 4b are not protonated in TFMSA. It is known that benzophenone moieties exist as protonated forms in TFMSA.$^{3,4}$ The measured chemical shift of the carbonyl carbon (C$_5$) in protonated benzophenone corresponds to that of 4b (Table S1), indicating that the carbonyl
group in 4b is protonated in TFMSA. Since the methoxy and carbonyl groups of 4b are in proximity, it is assumed that the proton on the methoxy group transfers to the carbonyl group aside from the proton transfer mechanism.

Table S1  $^{13}$C NMR chemical shifts

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<thead>
<tr>
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<th>Chemical shift (ppm)</th>
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<tbody>
<tr>
<td></td>
<td>$C_1$</td>
</tr>
<tr>
<td>4b</td>
<td>Measured value$^a$</td>
</tr>
<tr>
<td></td>
<td>Calculated Value$^b$</td>
</tr>
<tr>
<td>4c</td>
<td>Calculated Value$^b$</td>
</tr>
<tr>
<td>Protonated benzophenone</td>
<td>Measured value$^c$</td>
</tr>
</tbody>
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$^a$Measured in CF$_3$SO$_2$H at -20 °C. $^b$Calculated by DFT-DIAO. $^c$Measured in CF$_3$SO$_2$H at 25 °C.

Figures

Fig. S1 Relationship between the amount of the reactants (2 and 3) and the product (5) with the reaction time.
Fig. S2  Second-order kinetic plot for the model reaction between 2 and 3.

Fig. S3  $^{13}$C NMR DEPT-135 spectra of 5 (a) in DMSO-$d_6$ and (b) in TFMSA.
Fig. S4 $^{13}$C NMR spectra of 4 in TFMSA at 25 °C.

Fig. S5 $^1$H NMR spectra of (a) 7 and (b) the mixture of the model reaction between 6 and 3
Fig. S6 $^{13}$C NMR spectra of (a) 6 and (b) 7 in TFMSA.

Fig. S7 $^1$H NMR spectrum of polymer in DMSO-$d_6$. 
Fig. S8  TG curve of polymer under N\textsubscript{2}.

\[ T_{d5} = 354 \, ^\circ\text{C} \]

\[ T_g = 202 \, ^\circ\text{C} \]
Fig. S9  DSC curve of polymer.

![DSC curve of polymer](image)

**Fig. S10**  Stress-strain curve of polymer films cast from chloroform solution.

### References

1. M. J. Frisch et al., Gaussian 09, Revision E.01; Gaussian, Inc., Wallingford CT, 2009.

