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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 K_2CO_3 and used after recrystallization from acetonitrile. Trifluoromethanesulfonic acid (TFMSA), benzoic acid (**3**), benzoyl chloride, $AlCl_3$, 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 benzoyl 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%). ^1H NMR (DMSO-d_6, δ, 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, δ, 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%). ^1H NMR (DMSO-d_6, δ, 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, δ, 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_2CO_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, δ, 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, δ, 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, δ, 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, δ, 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-d_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-d_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,

$$-d[3]/dt = k_1[2][3] + k_2[4][3], \quad (1)$$

$$-d[2]/dt = k_1[2][3], \quad (2)$$

$$d[4]/dt = k_1[2][3] - k_2[4][3], \quad (3)$$

and

$$d[5]/dt = k_2[4][3]; \quad (4)$$

if $k_2 >> k_1$, the amount of the intermediate **4** can be ignored in the steady state. Thus,

$$d[4]/dt = 0. \quad (5)$$

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

$$[4] = k_1/k_2[2]. \quad (6)$$

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

$$d[5]/dt = k_1[2][3]. \quad (7)$$

The concentrations of **2** and **3** are given by

$[2] = [2]_0 - [5]$ and $[3] = [3]_0 - 2[5]$.

Therefore, the equation (7) is written as

$$d[5]/dt = k_1([2]_0 - [5])([3]_0 - 2[5]).$$

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

$$\ln([2]/[3]) = (2[2]_0 - [3]_0)k_1 t + \ln([2]_0/[3]_0).$$

Preparation of films for tensile tests

The polymer synthesized in the condition of $[\mathbf{2}]_0/[\mathbf{1}]_0 = 1.1$ ($M_w = 58{,}400$, $M_w/M_n = 1.7$) 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 x H = 5 x 40 mm) with about 50 μm thickness.

Calculation methods

The structures and ^{13}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}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 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

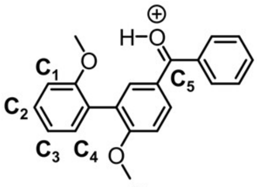
Calculation of ^{13}C NMR shifts

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.

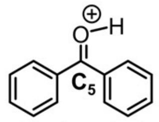
Table S1 ^{13}C NMR chemical shifts

		Chemical shift (ppm)				
		C_1	C_2	C_3	C_4	C_5
4b	Measured value[a]	113.10	129.67	120.20	131.34	201.48
	Calculated Value[b]	114.52	135.86	123.61	134.52	197.16
4c	Calculated Value[b]	115.11	134.88	134.31	137.90	192.45
Protonated benzophenone	Measured value[c]					207.87

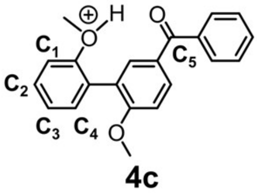
[a]Measured in CF_3SO_3H at -20 °C. [b]Calculated by DFT-DIAO.
[c]Measured in CF_3SO_3H at 25 °C.



4b



Protonated benzophenone



4c

Figures

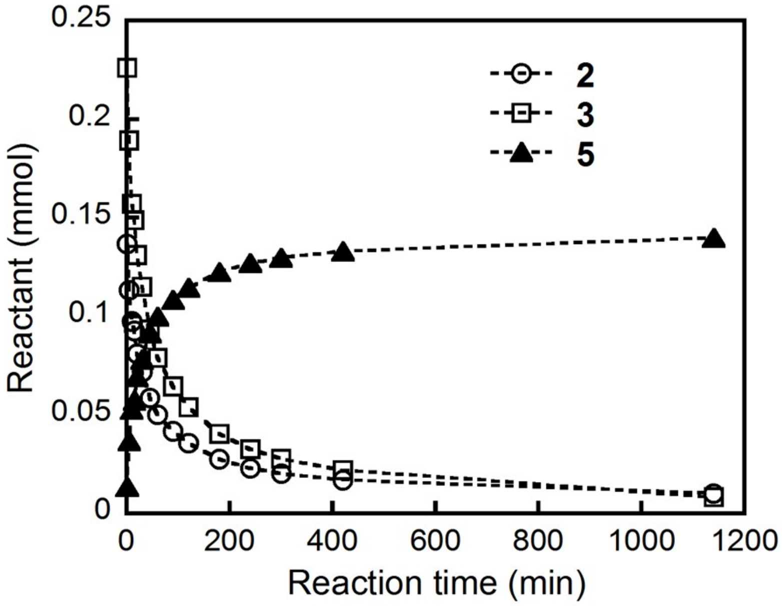


Fig. S1 Relationship between the amount of the reactants (**2** and **3**) and the product (**5**) with the reaction time.

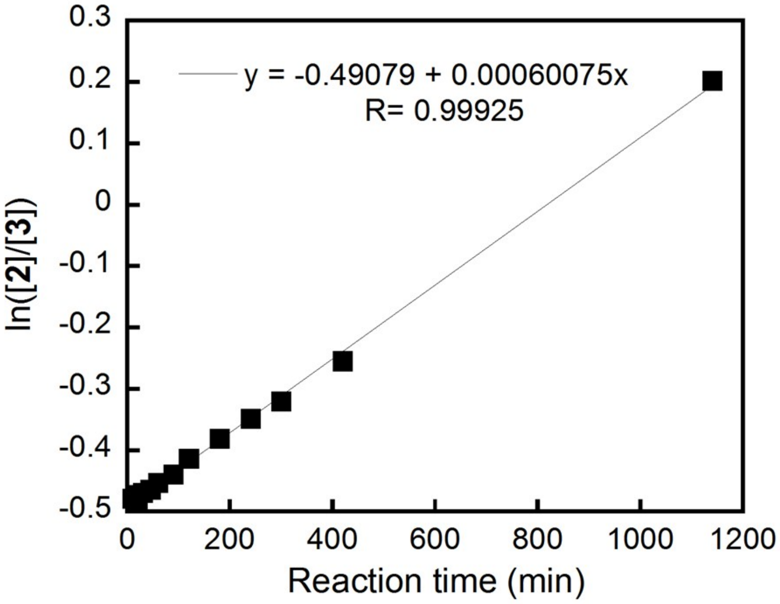


Fig. S2 Second-order kinetic plot for the model reaction between **2** and **3**.

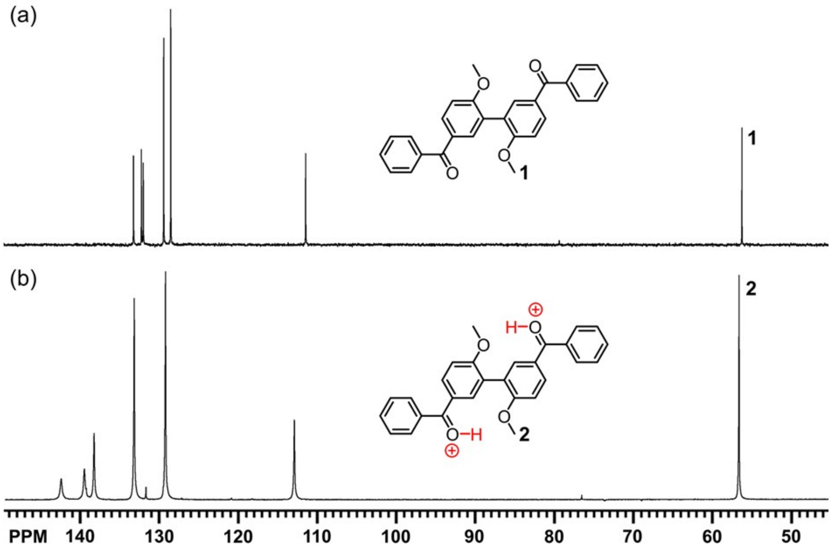


Fig. S3 ^{13}C NMR DEPT-135 spectra of **5** (a) in DMSO-d_6 and (b) in TFMSA.

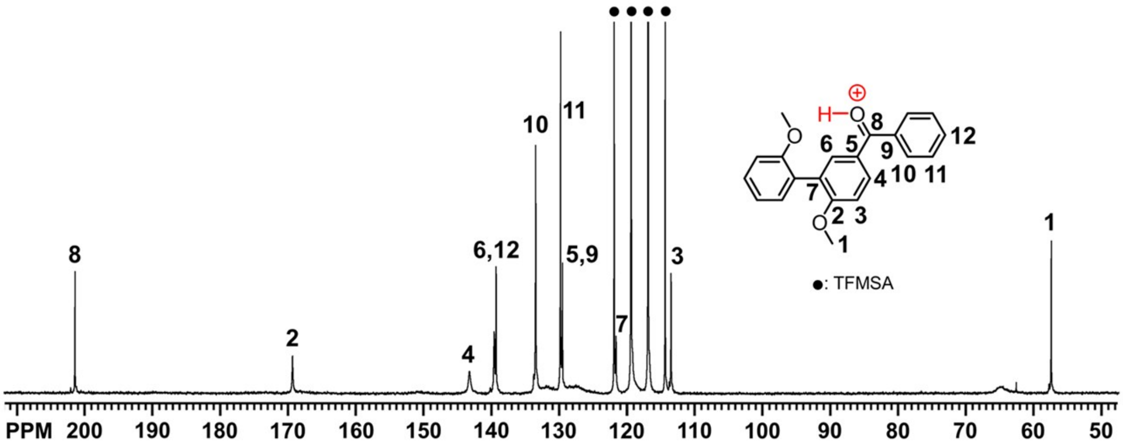


Fig. S4 ^{13}C NMR spectra of **4** in TFMSA at 25 ^{o}C.

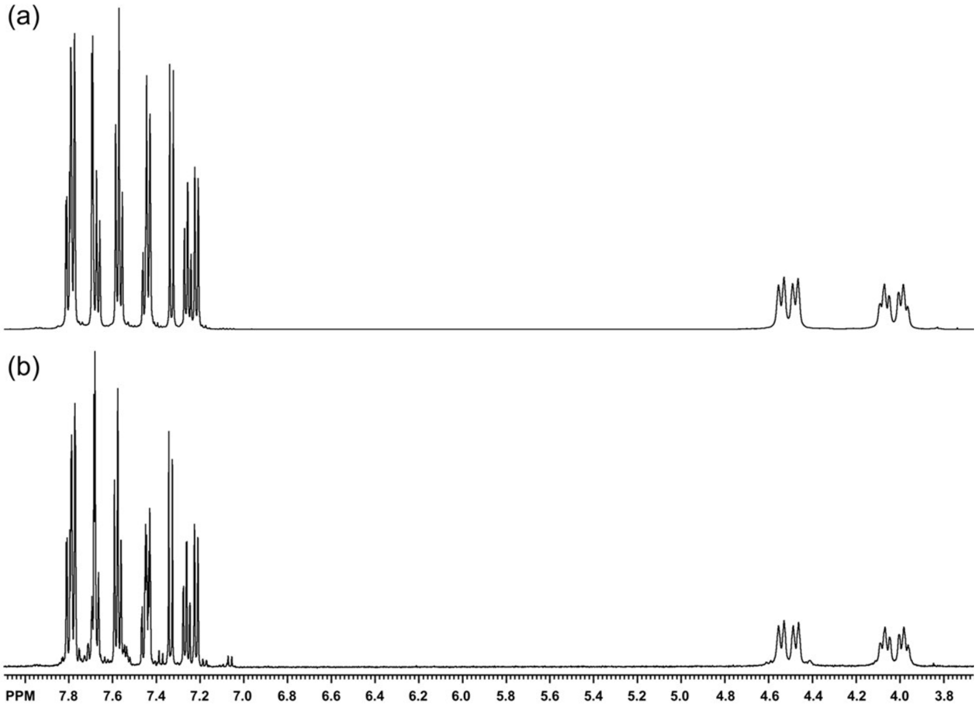


Fig. S5 ^{1}H NMR spectra of (a) **7** and (b) the mixture of the model reaction between **6** and **3**

in DMSO-d_6.

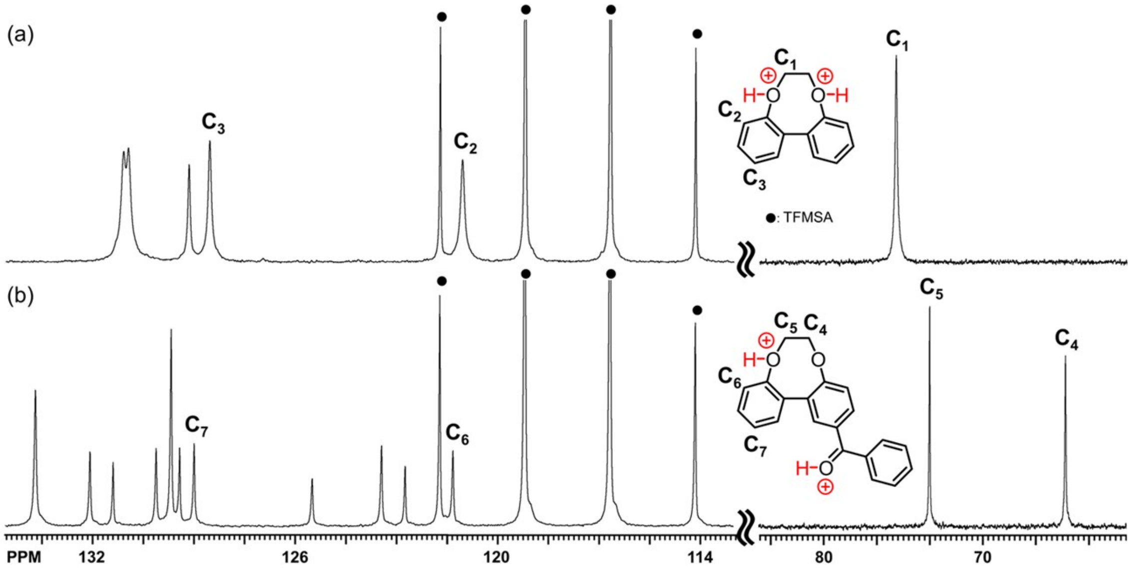


Fig. S6 ^{13}C NMR spectra of (a) **6** and (b) **7** in TFMSA.

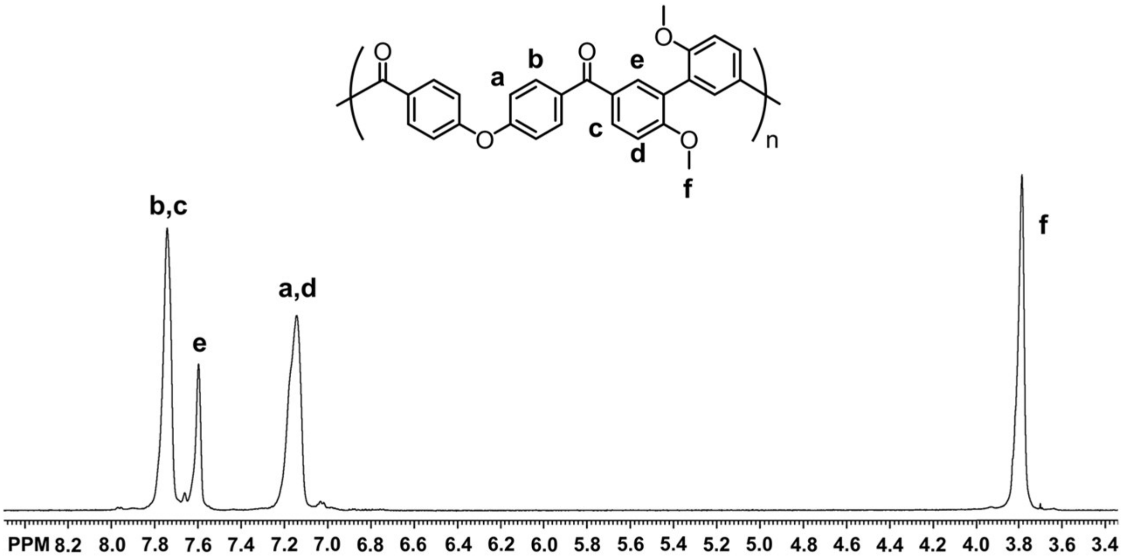


Fig. S7 ^{1}H NMR spectrum of polymer in DMSO-d_6.

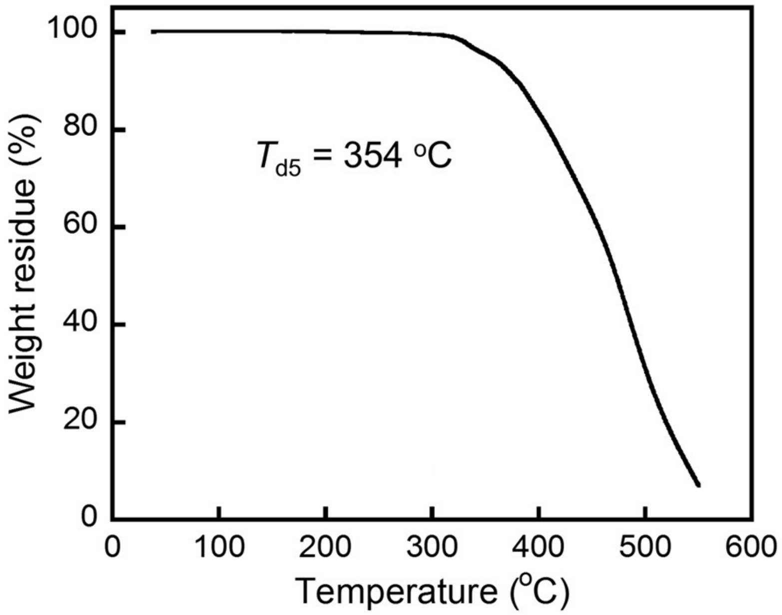


Fig. S8 TG curve of polymer under N_2.

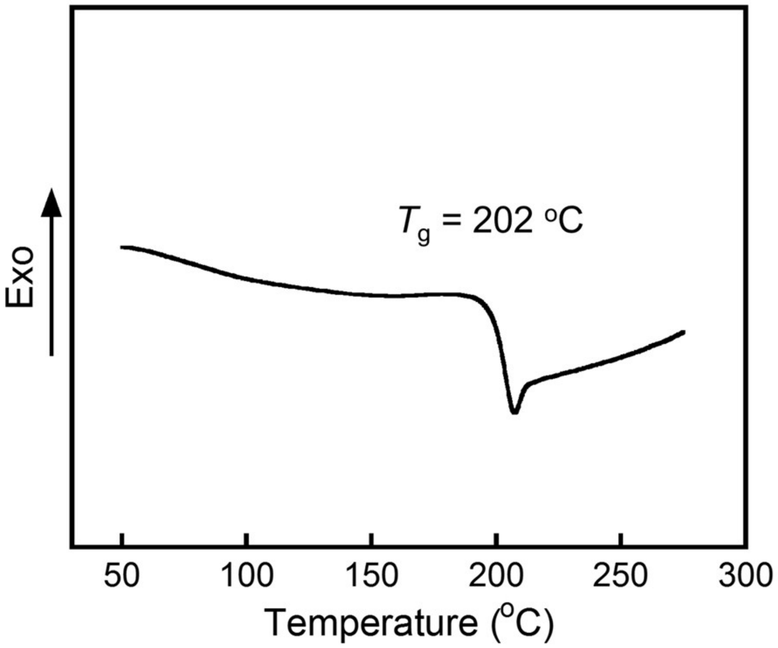


Fig. S9 DSC curve of polymer.

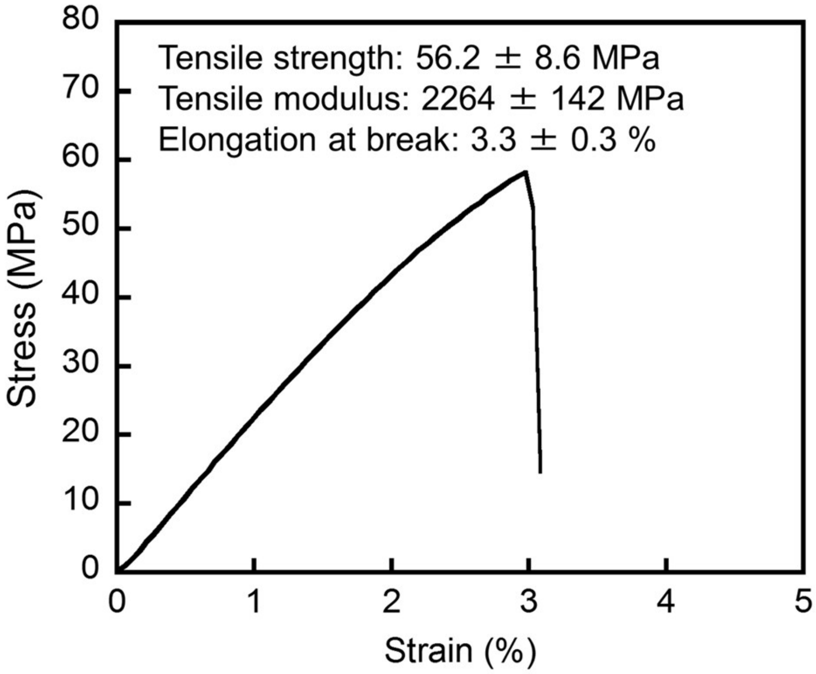


Fig. S10 Stress-strain curve of polymer films cast from chloroform solution.

References

1. M. J. Frisch et al., Gaussian 09, Revision E.01; Gaussian, Inc., Wallingford CT, 2009.
2. V. Vrček, O. Kronja and H. U. Siehl, *J. Chem. Soc., Perkin Trans. 2*, **1999**, 7, 1317-1322.
3. J. P. Hwang, G. S. Prakash and G. A. Olah, *Tetrahedron*, **2000**, 56, 7199-7203.
4. A. Kethe, A. F. Tracy and D. A. Klumpp, *Org. Biomol. Chem.*, **2011**, 9, 4545-4549.