Electronic Supplementary Information (ESI) for:

Synthesis of Aromatic Polyketones by Nonstoichiometric Friedel-Crafts Polycondensation Using $AlCl_3$

Kazuya Matsumoto*, Chisa Fukui, Riku Shoji, and Mitsutoshi Jikei

Department of Materials Science, Graduate School of Engineering Science, Akita University, 1-1 Tegatagakuen-machi, Akita-shi, Akita 010-8502, Japan

Corresponding Author

Kazuya Matsumoto* (E-mail : kmatsu@gipc.akita-u.ac.jp)

Materials and Methods

Materials

1,2-Dichloroethane (DCE) was purchased from FUJIFILM Wako Pure Chemical Corp. (Osaka, Japan) and distilled from calcium hydride before use. Nitromethane was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) and distilled from calcium hydride before use. 2,2'-Dihydroxybiphenyl (DMB) was prepared by dimethylation of 2,2'-dihydroxybiphenyl using iodomethane and K_2CO_3 and used after recrystallization from acetonitrile. $AlCl_3$ and benzoyl chloride (BzCl) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) and used as received. The conformationally fixed compound **5** and the monoacylated compound **6** were prepared according to the literature.[1]

Model reactions between DMB and BzCl

To a solution of DMB (0.107 g, 0.50 mmol) in a mixed solvent of DCE (1.6 mL) and nitromethane (0.4 mL) was added $AlCl_3$ (0.400 g, 3.0 mmol) at 0 °C under nitrogen. Then, BzCl (0.141 g, 1.0 mmol) was added to the mixture with stirring, and the stirring was continued for 3 h at 25 °C. The resulting mixture was diluted with chloroform and washed with 1 M HCl and saturated NaCl aqueous solution. After removal of solvents under reduced pressure, the residue was diluted by chloroform to perform thin-layer chromatography (left side in Fig. S2). The model reaction between BzCl and DMB was also conducted by stirring at 0 °C instead of 25 °C (right side in Fig. S2).

Model reaction between compound 5 and BzCl

To a solution of **5** (0.106 g, 0.50 mmol) in a mixed solvent of DCE (1.6 mL) and nitromethane (0.4 mL) was added $AlCl_3$ (0.333 g, 2.5 mmol) at 0 °C under nitrogen. Then, BzCl (0.070 g, 0.50 mmol) was added to the mixture with stirring, and the stirring was continued for 3 h at 0 °C. The resulting mixture was diluted with chloroform and washed with 1 M HCl and saturated NaCl aqueous solution. After removal of solvents under reduced pressure, the residue was diluted by deuterated dimethyl sulfoxide (DMSO-d_6) to carry out NMR measurements.

Measurements

^{1}H NMR spectra were recorded using a JEOL JNM-ECX 500 NMR spectrometer (Jeol Co., Tokyo, Japan). Gel permeation chromatographic (GPC) measurements were carried out using a Shodex RI-71S RI detector (Showa Denko K. K., Tokyo, Japan) and a Shodex LF804 polystyrene–divinylbenzene column (Showa Denko K. K., Tokyo, Japan) with chloroform as the eluent. Thermogravimetric analysis (TGA) measurements were carried out using a

STA7300 (Hitachi High-Tech Science Corp., Tokyo, Japan) at a heating rate of 10 °C min^{-1} under nitrogen flow (200 mL min^{-1}). Differential scanning calorimetry (DSC) measurements were carried out using a DSC7000X (Hitachi High-Tech Science Corp., Tokyo, Japan). The heating rate was set at 10 °C min^{-1}. Thin-layer chromatography was carried out using an aluminium plate with silica gel 60 F254 (Merck KGaA, Darmstadt, Germany).

Figures

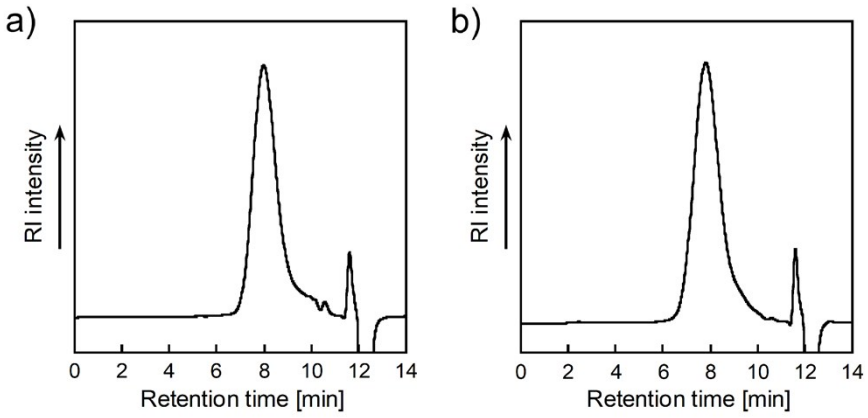

Fig. S1 Typical GPC curves of (a) polyketone **3** ($[DMB]_0/[TC]_0$ = 1.5 mol/mol) and (b) polyketone **4** ($[DMB]_0/[BDC]_0$ = 1.5 mol/mol).

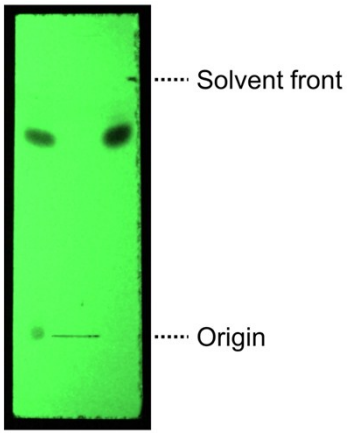

Fig. S2 Photograph of a thin-layer chromatography plate of the products in the model reactions at 25 °C (left side) and 0 °C (right side) illuminated by 254 nm light (developing solvent: chloroform/ethyl acetate = 10/1 (v/v)). The bottom spot in the left side shows the existence of polar side products.

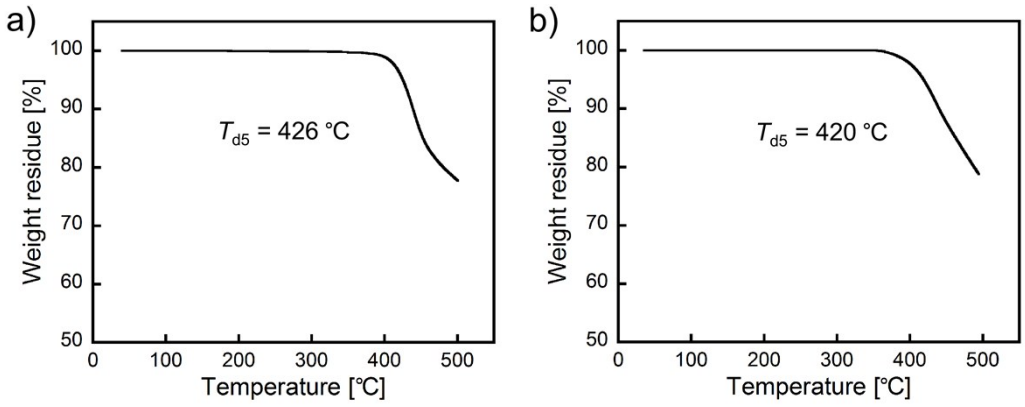

Fig. S3 TG curves of (a) polyketone **3** and (b) polyketone **4** under N_2.

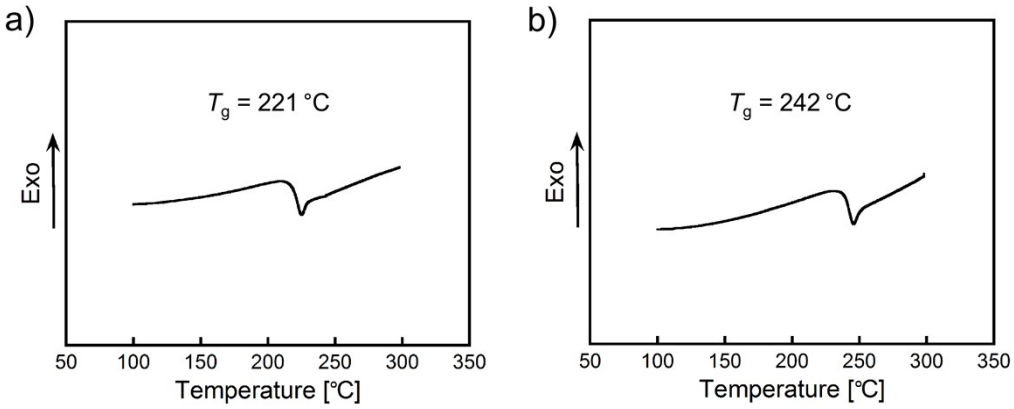

Fig. S4 DSC curves of (a) polyketone **3** and (b) polyketone **4**.

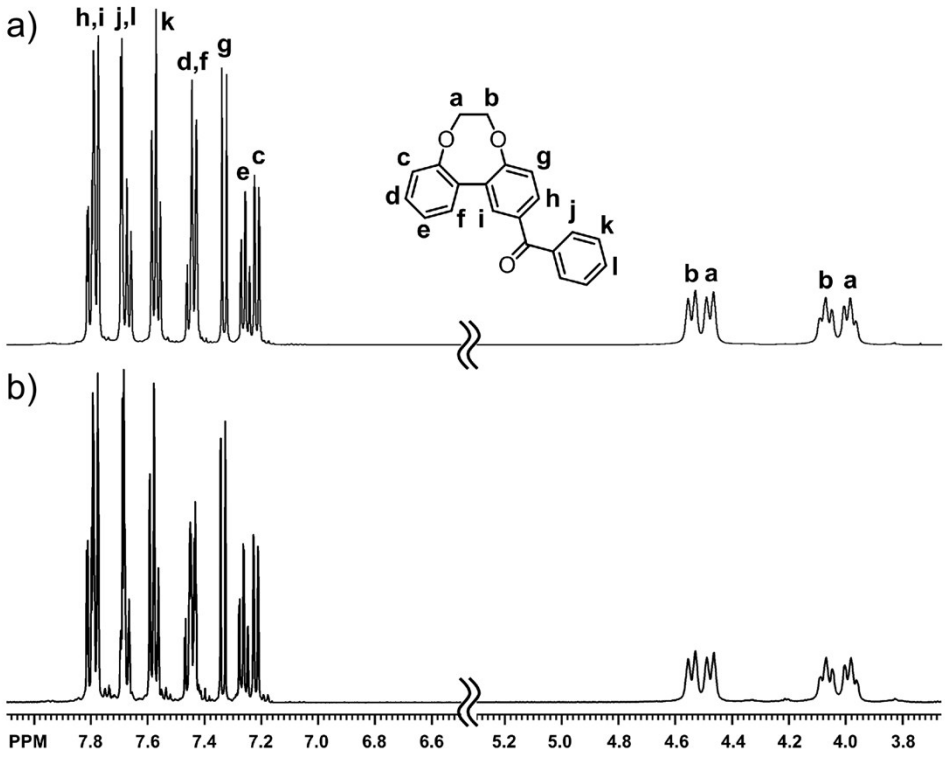

Fig. S5 ^{1}H NMR spectra of (a) compound **6** and (b) the product of the model reaction between **5** and BzCl in DMSO-d_6.

References

1. K. Matsumoto, T. Ogawa and M. Jikei, *Polym. Chem.*, 2017, **8**, 7297–7300.