

Direct Synthesis of Active Diesters From Dicarboxylic Acids and Phenols

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Supporting Information

Figure 1S. ^1H NMR spectrum of *p*-nitrobenzoate

Figure 2S. ^1H NMR spectrum of 4,4'-oxybis(*p*-nitrophenylbenzoate)

Figure 3S ^1H NMR spectrum of poly(*o*-hydroxyamide)

Figure 4S FT-IR spectrum of poly(*o*-hydroxyamide)

Measurement. Infrared spectra (FTIR) were taken with a Horiba FT-210 spectrophotometer. The ^1H nuclear magnetic resonance (NMR) spectra were recorded on a BRUKER GPX300 spectrometer (^1H at 300 MHz). M_n and M_w were determined by GPC with JASCO PU-2080Plus with two polystyrene gel columns (TSK GELs; GMH_{HR}-M) at 40 °C in DMF at a flow rate of 1.0 mL/min, calibrated with polystyrene standards. Elemental analysis were performed by a YANACO CHN corder MT-6 in Tokyo Institute of Technology Center for Advanced Materials Analysis.

Materials. Heptane, octane, cyclooctane, and nonane were obtained commercially and use as received. *N*-Methyl-2-pyrrolidinone (NMP) was purified by vacuum distillation. 4,4'-(Hexafluoroisopropylidene)bis(*o*-aminophenol) was recrystallized from tetrahydrofuran and hexane.

Preparation of *p*-nitrobenzoate

4-Nitrophenol (15 mmol, 2.1 g), benzoic acid (10 mmol, 1.2 g), and *p*-toluenesulfonic acid monohydrate (1.0 mmol, 0.19 g) were placed in a 50 mL two-necked round-bottom flask equipped with a Dean-Stark apparatus and condenser (Figure 1). The solvent (20 mL) was added and the mixture was refluxed under nitrogen. Reaction was monitored by IR spectroscopy, and the solvent was then removed by evaporation. The residue dissolved in NMP (50 mL) was reprecipitated in aqueous sodium bicarbonate solution (500 mL). The precipitate was dried *in vacuo* at 50 °C for 12 h. M.p. 142-143°C (lit.142-144°C. J. Org. Chem.1985,50,560). Anal. Calcd for C₁₃H₉NO₄: 243.21. C, 64.20; H, 3.73; N, 5.76; O, 26.31. Found: C, 64.69; H, 3.83; N, 5.67; O, 25.81.

IR (KBr): ν (cm⁻¹)=1739 (C=O), 1592 (Ar, C-H), 1519 (NO₂), 1346 (NO₂). ¹H-NMR (300 MHz, CDCl₃) δ (ppm)=7.43 (d, ArH, 2H), 7.55 (t, ArH, 2H), 7.69 (t, ArH, 1H), 8.21 (d, ArH, 2H), 8.33 (d, ArH, 2H).

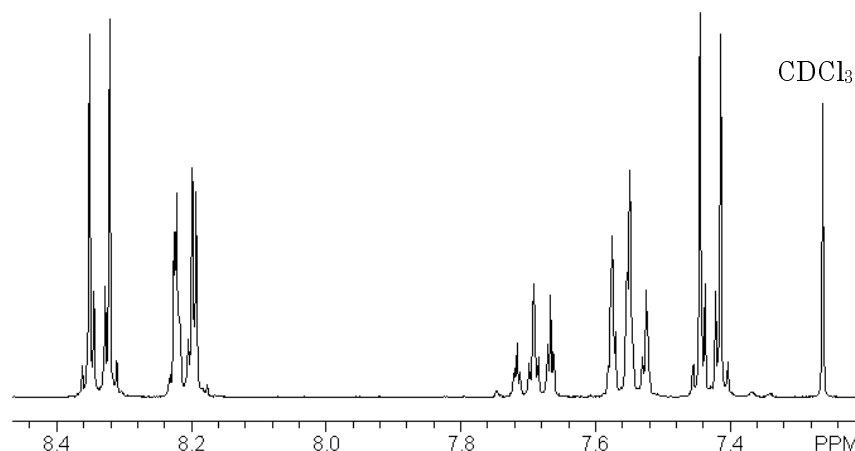


Figure 1S. ¹H NMR spectrum of *p*-nitrobenzoate.

Preparation of 4,4'-oxybis(*p*-nitrophenyl benzoate)

4-Nitrophenol (40 mmol, 5.5 g), 4,4'-oxybis(benzoic acid) (10 mmol, 2.6 g), and *p*-toluenesulfonic acid monohydrate (1.0 mmol, 0.19 g) were placed in a 100 mL two-necked round-bottom flask equipped with a Dean-Stark apparatus and a condenser. The reaction was carried out as described above. The product was recrystallized from toluene to produce pale orange needles. M.p. 208-210°C. Anal. Calcd for C₂₆H₁₆N₂O₉: 500.41. C, 62.40; H, 3.22; N, 5.60; O, 28.78. Found: C, 62.60; H, 3.59; N, 5.43; O, 28.38. IR (KBr): ν (cm⁻¹)=1731 (C=O), 1592 (Ar, C-H), 1523 (NO₂), 1349 (NO₂), 1241 (Ar-O-Ar). ¹H-NMR (300 MHz, DMSO-d₆) δ (ppm)=7.38 (d, ArH, 4H), 7.68 (d, ArH, 4H), 8.30 (d, ArH, 4H), 8.41 (d, ArH, 4H)

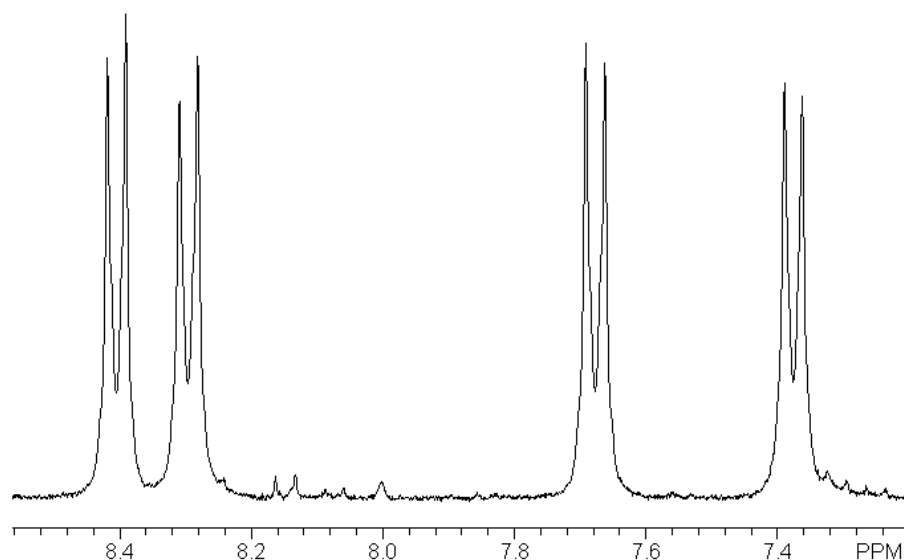


Figure 2S. ¹H NMR spectrum of 4,4'-oxybis(*p*-nitrophenylbenzoate).

Synthesis of poly(*o*-hydroxyamide)

4,4'-(Hexafluoroisopropylidene)bis(*o*-aminophenol) (1.00 mmol, 0.366 g) in NMP (2.8 mL) were placed in a 10 mL round-bottom flask. To this solution was added active ester **1** (1.00 mmol, 0.500 g) and 1-hydroxybenzotriazole monohydrate (0.40 mmol, 0.063 g) at room temperature. This solution was stirred at 90 °C for 72 h. The resulting polymer solution was poured into aqueous sodium bicarbonate solution (200 mL). The obtained precipitate was dissolved in NMP, and the solution was poured into H₂O / methanol solution (1/1 in volume, 200mL). The precipitate was filtered and dried *in vacuo* at 100 °C for 12 h.

IR (Film): ν (cm⁻¹)=1654 (C=O), 1596 (Ar, C-H), 1245 (Ar-O-Ar). ¹H-NMR (300 MHz, DMSO-d₆) δ (ppm)=7.04 (s, ArH, 4H), 7.22 (d, ArH, 4H), 7.98 (s, ArH, 2H), 8.07 (d, ArH, 4H), 9.55 (s, NHCO, 2H), 10.26 (s, ArOH, 2H).

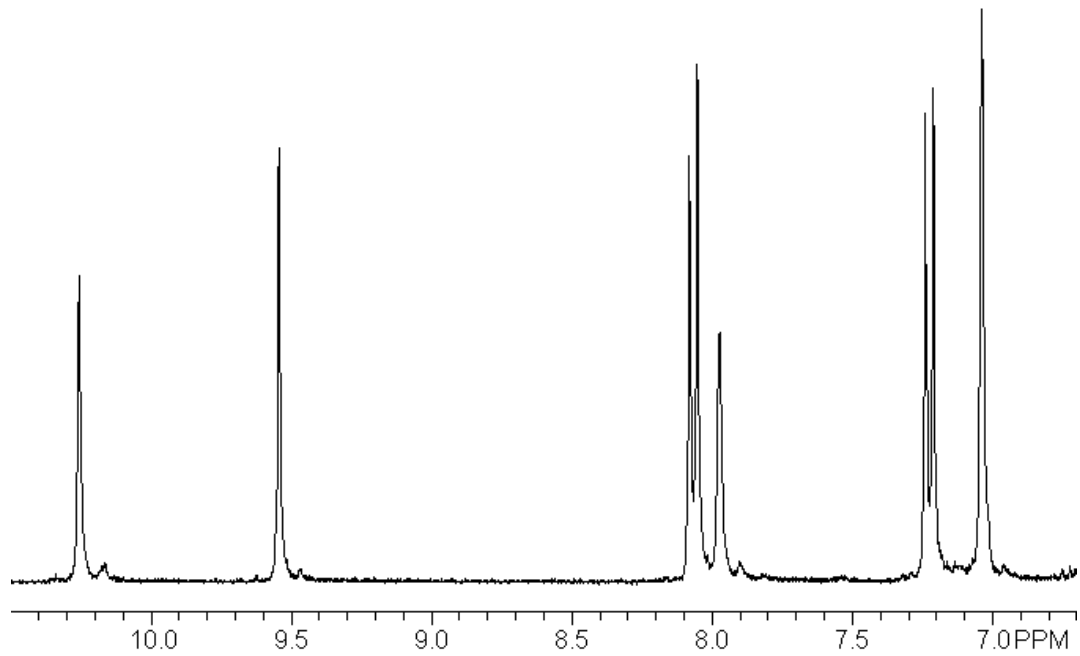


Figure 3. ^1H NMR spectrum of poly(*o*-hydroxyamide).

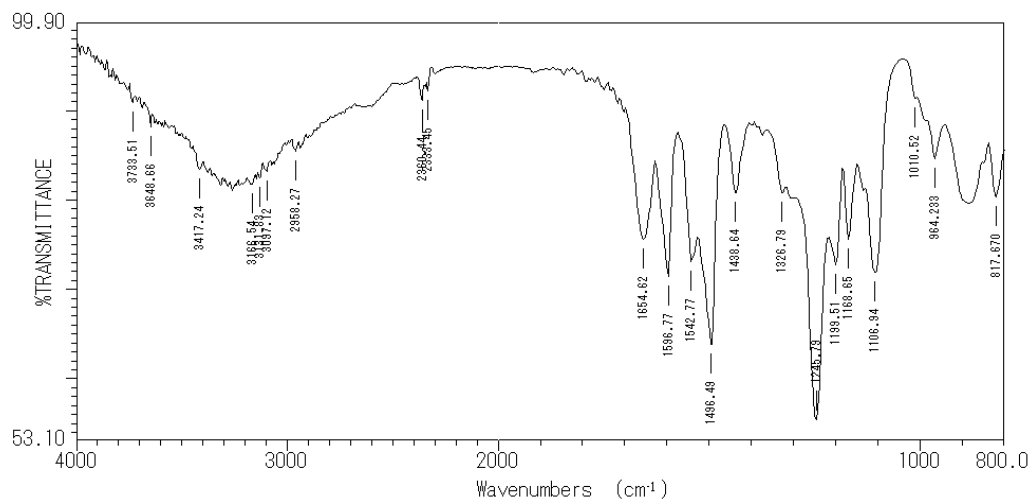


Figure 4S FT-IR spectrum of poly(*o*-hydroxyamide)