

Synthesis of Aramids by Polycondensation of Aromatic Dicarboxylic Acids with Aromatic Diamines Containing Ether Linkages

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Supporting Information

Syntheses and characterization of model compound **3** and polyamide **6ab'**.

Measurement. FT-IR spectra were measured on a Horiba FT-720 spectrometer. ^1H and ^{13}C NMR spectra were recorded with a Bruker DPX300S spectrometer. Number- and weight-average molecular weights (M_n and M_w) were measured by gel permeation chromatography (GPC) on a JASCO PU-2080Plus system equipped with two polystyrene gel column (TSKGELS ; GMH_{HR}-M). *N,N*-Dimethylformamide (DMF) containing 0.01 M LiBr was used as a solvent at a flow rate of 1.0 mL min⁻¹. M_n and M_w were calibrated by standard polystyrene samples. Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating rate of 10 °C/min for thermogravimetry (TG) and SEIKO INSTRUMENTS Inc. EXSTAR6000 DSC6200 thermal analyzer at a heating rate of 10 °C/min for differential scanning calorimetry (DSC).

Materials. 4,4'-hexafluoroisopropylidenebis(*p*-phenyleneoxy)dianiline (**5b**), 4,4'-(*m*-phenylenedioxy)dianiline (**5b'**) and 3,4'-oxydianiline (**5b''**) were purchased from Tokyo Chemical Industry Co. 4,4'-hexafluoroisopropylidene-bis(benzoic acid) (**4a**) purchased from Aldrich Chem. Co., was recrystallized from acetonitrile prior to use. 4,4'-(*m*-phenylenedioxy)-bis(benzoic acid) (**4a'**)¹ was synthesized according to the literature. Isophthalic acid (**4a''**) purchased from Tokyo Chemical Industry Co., was recrystallized from ethanol prior to use. The other reagents and solvents were obtained commercially and used as received.

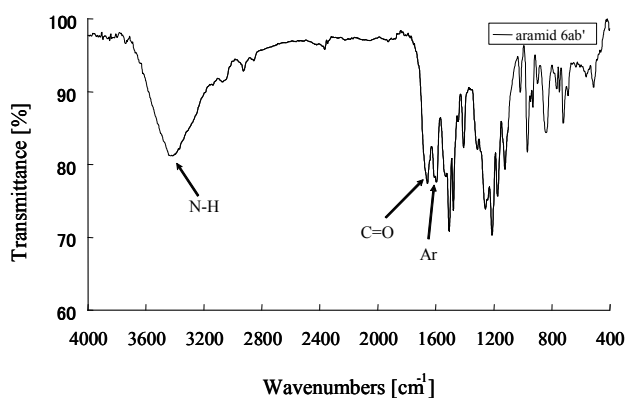
Model reaction

Benzoic acid (0.368 g, 3.01 mmol) and 4,4'-oxydianiline (0.204 g, 1.02 mmol) were added to a Pyrex

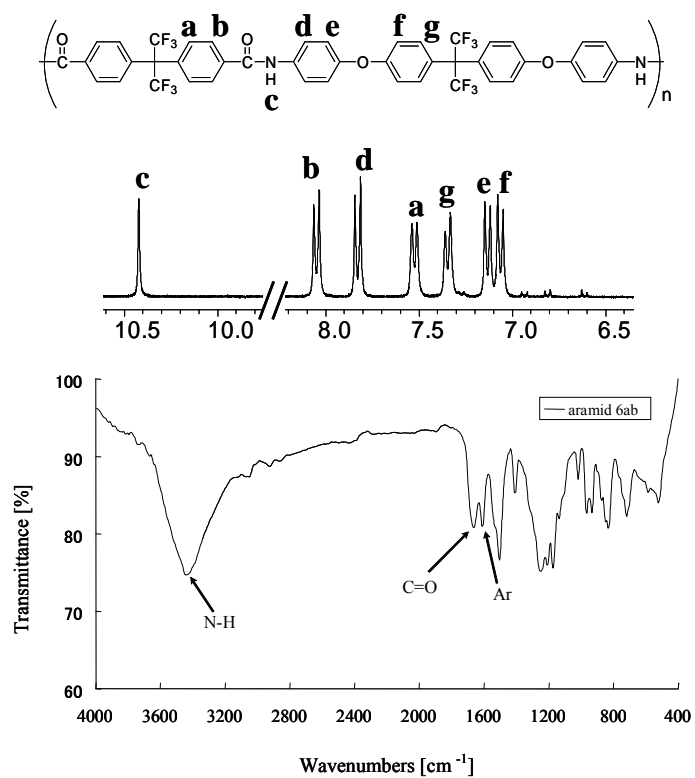
test tube (15 mL) equipped with a nitrogen gas inlet and outlet tubes. The mixture was heated in oil bath at 200 or 230 °C under a nitrogen atmosphere for 5 h, and then allowed to cool to room temperature. The solids were dissolved in DMF (3 mL), and the resulting solution was poured into a 3% NaHCO₃ solution (300 mL) to remove the excess of benzoic acid. The precipitate was collected, dried in *vacuo* at 120 °C for 1 d. The yield of model compound was 0.402 g (97%): m.p. 266.6-267.6 (lit.² 266-267 °C). IR (KBr), ν (cm⁻¹): 3325 (-NH), 1651 (C=O). ¹H NMR (DMSO, δ , ppm, 40 °C): 10.2 (s, N-H, 1H), 7.96 (d, J=6.9, ArH, 4H), 7.79 (d, J=9.0, ArH, 4H), 7.62-7.50 (m, ArH, 6H), 7.02 (d, J=9.0, ArH, 4H).

Synthesis of polyamide 6ab'

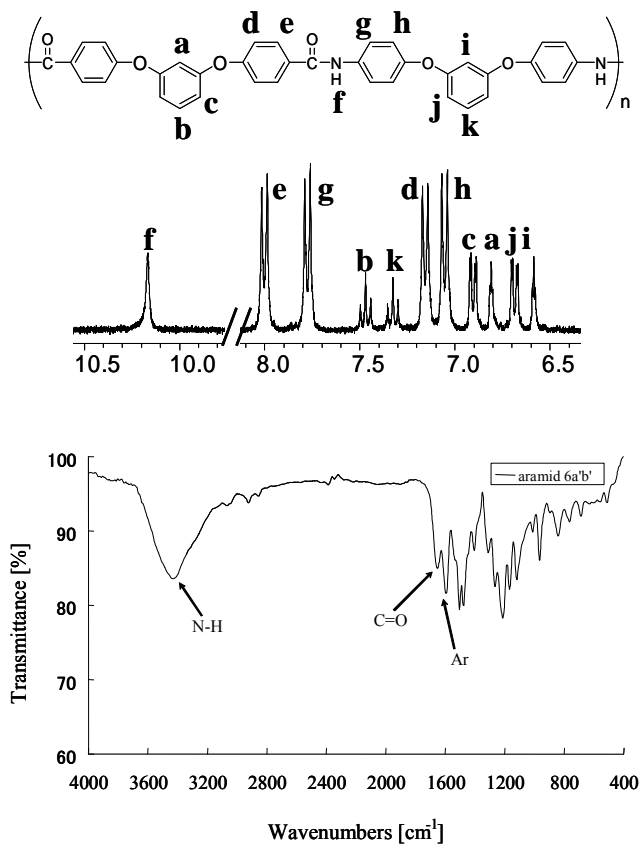
In a 15 mL Pyrex tube equipped with a stirring bar and nitrogen gas inlet and outlet tubes, were placed 4,4'-hexafluoroisopropylidenebis(benzoic acid) (monomer **4a**; 0.196 g, 0.50 mmol) and 4,4'-(*m*-phenylenedioxy)dianiline (monomer **5b'**; 0.146 g, 0.50 mmol) under a stream of nitrogen. The mixture was gradually heated up to 130 °C and kept at this temperature for 0.5 h, heated at 170 °C for 0.5 h, 200 °C for 2 h, and 300 °C for 7 h, respectively, with a heating mantle, and then allowed to cool to room temperature. The solid was dissolved in NMP (3 mL), and the solution was poured into methanol (300 mL). The polymer was collected, and dried in *vacuo* at 120 °C for 1 d. The yield of polymer **6ab'** was 0.257 g (76%). IR (KBr), ν (cm⁻¹): 3429 (-NH), 1658 (C=O). ¹H NMR (DMSO, δ , ppm, 40 °C) : 10.4 (s, N-H, 1H), 8.03 (d, J=8.7, ArH, 4H), 7.79 (d, J=9.0, ArH, 4H), 7.51 (d, J=8.4, ArH, 4H), 7.34 (t, J=8.4, ArH, 1H), 7.08 (d, J=9.0, ArH, 4H), 6.70 (dd, J=8.3, 2.1, ArH, 2H), 6.60 (t, J=2.7, ArH, 1H). *Anal.* Calcd. For C₃₅H₂₂N₂: C, 64.82 ; H, 3.42 ; N, 4.32. Found: C, 64.56 ; H, 3.77 ; N, 4.22.



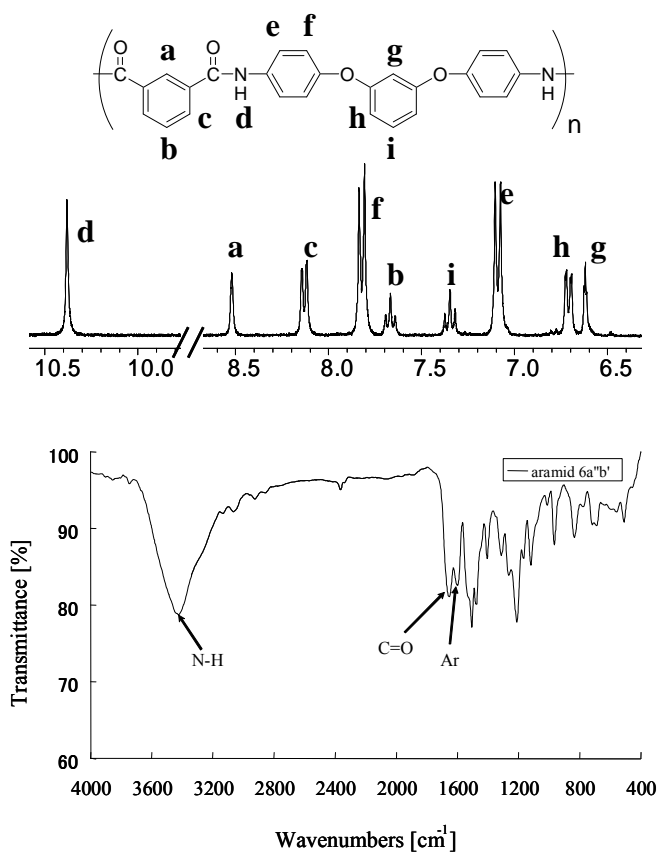
polyamide **6ab**



polyamide **6a'b'**



polyamide **6a''b'**



References

1. G.C. Eastmond, J. Paprotny, and R.S. Irwin, *Polymer* 40, 46 (1999).
2. G. M Tseitlin, *Zhurnal Organicheskoi Khimii.*, 18(5), 1075 (1982).