Synthesis of Aramids by Bulk Polycondensation of Aromatic Dicarboxylic Acids with 4,4’-Oxydianiline

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Experimental supplements

**Fig. S1** A) FT-IR and B) \textsuperscript{1}H NMR spectra of aramid 4a.

Polycondensation of aramid 4b

The title aramid 4b, was synthesized according to the same procedure as 4a performed with 0.392 g (1.00 mmol) of 1b and 0.220 g (1.10 mmol) of 2. After the reaction, the aramid 4b (0.551 g, 99% yield) was isolated as a light blue fiber. IR (KBr), \( \nu \) (cm\(^{-1}\)): 3440 (N–H, amide), 1658 (C=O, amide). \textsuperscript{1}H NMR (300 MHz, DMSO-\( d_6 \), \( \delta \), ppm, 40 °C): 10.3 (s, N–H, 2H), 8.04 (d, J=8.5 Hz, ArH, 4H), 7.80 (d, J=9.0 ArH, 4H), 7.52 (d, J=7.9 Hz, ArH, 4H), 7.03 (d, J=8.9 Hz, ArH,}
Fig. S2 A) FT-IR and B) $^1$H NMR spectra of aramid 4b.

Polycondensation of aramid 4c

The title aramid 4c, was synthesized according to the same procedure as 4a performed with 0.258 g (1.00 mmol) of 1c and 0.220 g (1.10 mmol) of 2. After the reaction, the aramid 4c (0.406 g, 97% yield) was isolated as a light blue fiber. IR (KBr), $\nu$ (cm$^{-1}$): 3293 (N–H, amide), 1650 (C=O, amide). $^1$H NMR (300 MHz, DMSO-$d_6$, $\delta$, ppm, 40 °C): 10.2 (s, N–H, 2H), 8.09 (d, $J$=8.5 Hz, ArH, 4H), 7.80 (d, $J$=8.9 Hz, ArH, 4H), 7.25 (d, $J$=7.2 Hz, ArH, 4H), 7.07 (d, $J$=8.8 Hz, ArH, 4H).

Fig. S3 A) FT-IR and B) $^1$H NMR spectra of aramid 4c. *These signals were assigned to the protons from terminal groups of oligomer because aramid 4c had the low solubility in DMSO.
Synthesis of 3-(4-phenoxyphenylcarbamoyl)benzoic acid (5)

To a solution of isophthaloyl dichloride (1.00 g, 4.96 mmol) in dehydrated NMP (20 mL), a solution of 4-phenoxyaniline (1.03 g, 5.56 mol) in dehydrated NMP (10 mL) was slowly added at 0 °C under a nitrogen atmosphere. The reaction mixture was warmed up to room temperature, then stirred for 1 h. After the reaction, the resulting solution was poured into NaOHaq (500 mL, 3 wt%). The precipitate, which was diamide as a byproduct, was removed by filtration, and then the solution was acidified by conc. HCl to produce 5 as a solid. The precipitate was collected by filtration and dried under the reduced pressure. The resulting solid was purified by recrystallization from ethyl acetate and hexane (6/4, v/v) to obtain 5 as a white crystal (0.458 g, 28% yield).

IR (KBr), ν (cm⁻¹): 3282 (N–H, amide), 1689 (C=O, carboxylic acid), 1643 (C=O, amide). ¹H NMR (300 MHz, DMSO-d₆, δ, ppm, 40 °C): 13.1 (br s, –COOH, 1H), 10.4 (s, N–H, 1H), 8.55 (s, ArH, 1H), 8.20 (d, J=8.4 Hz, ArH, 1H), 8.15 (d, J=8.4 Hz, ArH, 1H), 7.81 (d, J=9.0 Hz, ArH, 2H), 7.66 (t, J=7.8 Hz, ArH, 1H), 7.38 (t, J=8.0 Hz, ArH, 2H), 7.11 (t, J=7.2 Hz, ArH, 1H), 7.07-6.98 (m, ArH, 4H). ¹³C NMR (75 MHz, DMSO-d₆, δ, ppm, 40 °C): 166.7, 164.5, 157.2, 152.3, 135.2, 134.7, 131.9, 131.7, 131.0, 129.8, 128.6, 128.3, 122.9, 122.1, 119.0, 117.9. m.p. 270.6 °C with the decomposition (measured by TG/DTA). Anal. Calcd. For C₂₀H₁₅N: C, 72.06; H, 4.54; N, 4.20. Found: C, 72.06; H, 4.64; N, 4.07.

Synthesis of N-(4-(4-nitrophenoxy)phenyl)benzamide
To a solution of 4-amino-4′-nitorodiphenyl ether (1.16 g, 5.05 mmol) in dehydrated NMP (10 mL), benzoyl chloride (1.25 mL, 10.8 mmol) was slowly added at 0 °C under a nitrogen atmosphere. The reaction mixture was warmed up to room temperature, then stirred for 1 h. After the reaction, the solution was poured into NaHCO₃ aq (300 mL, 5 wt%). The precipitate was collected by filtration, and then purified by recrystallization from ethyl acetate to give the titled compound as a brown crystal which was a desired product (1.47 g, 87% yield).

IR (KBr), ν (cm⁻¹): 3344 (N–H, amide), 1651 (C=O, amide), 1523, 1342 (–NO₂). ¹H NMR (300 MHz, DMSO-d₆, δ, ppm, 40 °C): 10.3 (s, N–H, 1H), 8.24 (d, J=9.3 Hz, ArH, 2H), 7.98 (d, J=6.6 Hz, ArH, 2H), 7.92 (d, J=9.0 Hz, ArH, 2H), 7.62–7.51 (m, ArH, 3H), 7.19 (d, J=9.0 Hz, ArH, 2H), 7.13 (d, J=9.0 Hz, ArH, 2H). ¹³C NMR (75 MHz, DMSO-d₆, δ, ppm, 40 °C): 165.4, 163.1, 149.7, 142.0, 136.5, 134.8, 131.4, 128.2, 127.5, 125.9, 122.1, 120.5, 116.9. m.p. 213.1–214.2 °C.

Anal. Calcd. For C₁₉H₁₄N₂: C, 68.26; H, 4.22; N, 8.38. Found: C, 68.28; H, 4.37; N, 8.30.

Synthesis of N-(4-(4-aminophenoxy)phenyl)benzamide (6)

A mixture of N-(4-(4-nitrophenoxy)phenyl)benzamide (0.616 g, 1.84 mmol) and 10% Pd/C (0.0217 g) in tetrahydrofuran (10 ml) was stirred at room temperature for 24 h under hydrogen atmosphere. The solution was filtered through Celite, concentrated, and purified by recrystallization from ethyl acetate and hexane (7/3, v/v) to give the desired compound 6 as a pale red solid (0.378 g, 67% yield).
IR (KBr), $\nu$ (cm$^{-1}$): 3402 (N–H, amide), 3344 (N–H, amine), 1651 (C=O, amide). $^1$H NMR (300 MHz, DMSO-$d_6$, $\delta$, ppm, 40 ºC): 10.1 (s, N–H, 1H), 7.96 (d, J=6.6 Hz, ArH, 2H), 7.70 (d, J=9.0 Hz, ArH, 2H), 7.60–7.49 (m, ArH, 3H), 6.89 (d, J=9.0 Hz, ArH, 2H), 6.77 (d, J=8.4 Hz, ArH, 2H), 6.62 (d, J=9.0 Hz, ArH, 2H), 4.86 (br s, –NH$_2$, 2H). $^{13}$C NMR (75 MHz, DMSO-$d_6$, $\delta$, ppm, 40 ºC): 165.1, 154.7, 146.3, 145.0, 134.9, 133.4, 131.2, 128.1, 127.4, 121.9, 120.2, 116.8, 114.8. m.p. 171.7–172.5 ºC. Anal. Calcd. For C$_{19}$H$_{16}$N$_2$: C, 74.98; H, 5.30; N, 9.20. Found: C, 74.90; H, 5.47; N, 9.04.

![Graph](image)

**Fig. S4** TG/DTA curve for oligo-aramid 3a.