Preparation and Helical Folding of Long-Chain Aromatic Polyamides

Jinxin Cao, a,b Mark Kline, c Zhongzhu Chen, a,b Bao Luan, a,b Menglan Lv, a,b Wenrui Zhang, a,b Chunxia Lian, a Qiwei Wang, a Qingfei Huang, a,b Xiaoxi Wei, c Jingen Deng, a Jin Zhu * a and Bing Gong *cd

a Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, 610041, China
b Graduate University of Chinese Academy of Sciences, Beijing 100049, China
c Department of Chemistry, University at Buffalo, State University of New York, Buffalo, NY 14260, USA
d College of Chemistry, Beijing Normal University, Beijing 100875, China

Supporting Information

Contents

I. Synthetic Procedures and Analytical Data------------------------------------------ 2
II. GPC Data of 3a, 3b and 3c---------------------------------------------------- 4
III. 1D 1H and 13C NMR Spectra of New Compounds--------------------------------- 7
IV. Concentration-Dependent 1H NMR Spectra of 3a, 3b, 3c and 4----------------- 9
V. UV Spectra of 3a, 3b, 3c and 4----------------------------------------------- 11
VI. Additional CD spectra-------------------------------------------------------- 14
I. Synthetic Procedures and Analytical Data

Chemicals were purchased from commercial sources and used as received. Unless otherwise specified, all solvents were removed with a rotary evaporator. Silica gel for analytical thin layer chromatography (TLC) and column chromatography (200–300 mesh) were purchased from Qingdao Haiyang Chemical Co., Ltd & Spegial Silica Gel Factory. The $^1$H NMR spectra were recorded at 300 MHz and $^{13}$C NMR spectra were measured at 75 MHz on a Bruker-300 spectrometer at ambient temperature using CDCl$_3$ or DMSO-$d_6$ as solvent (Cambridge Isotope Laboratories, Inc.). Chemical shifts are reported in parts per million downfield from TMS (tetramethylsilane). Coupling constant in $^1$H NMR are expressed in Hertz. Electrospray ionization high resolution mass spectra (ESI-HRMS) were recorded on a Bruke P-SIMS-Gly FT-ICR mass spectrometer. Circular Dichroism (CD) were recorded on a JASCO J-815 spectrometer. Gel Permeation Chromatography were recorded on a SHMADZU SPD-20A.

I-1. Preparation of polyamide 3

![Diagram of the reaction](image)

Diamine 6 (415 mg, 2 mmol), prepared from the reaction of 3, 5-dinitrobenzoyl chloride and isobutylamine followed by hydrogenation, was dissolved in 16 mL of N, N-dimethylacetamide (DMA) that treated by drying over CaH$_2$ and then being distilled, in a round-bottomed flask. After adding Et$_3$N (1.08 mL, 6 mmol), the solution was purged with N$_2$ a few times and then stirred in an ice-bath for 10 min, to which a solution of diacid chloride 7 (982 mg, 2 mmol), prepared based on known procedures,$^1$ in 16 mL of DMA was added rapidly. The reaction mixture was purged a few more times with nitrogen, and was then let to warm to room temperature and stirred for an additional 8 hrs. After removing solvent, the remaining residue was dissolved/suspended into CH$_2$Cl$_2$, washed with brine for three times, and dried over Na$_2$SO$_4$. Removing solvent led to 3 (1.12 g) as a light yellow powder. Using gel permeation chromatography (GPC), the weight-average molecular weights ($M_w$) of 3 was determined 14,746, with a molecular-weight dispersity of 6.80.
Oligoamides 4 and 5 were synthesized in good yields based on known synthetic procedures.\(^1\)

**Compound 4.** \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 9.96 (2 H, s), 8.78 (2 H, s), 8.49 (1 H, s), 7.88 (2 H, s), 6.63 (1 H, t, \(J = 6.0\) Hz), 6.52 (2 H, s), 4.21 ~ 4.10 (8 H, m), 4.02 ~ 3.89 (4 H, m), 3.85(6H, s), 3.64 ~ 3.50 (8 H, m), 3.28-3.24 (2 H, m), 1.94-1.89 (1H, m), 1.71- 1.57 (4H, m), 1.47~1.42 (10 H, m), 1.38~1.24(10 H, m), 0.97(6H, d, \(J=6.6\)), 0.88(12H, d, \(J=6.6\)), 0.72 (12 H, d, \(J = 6.6\) Hz). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 166.7, 165.1, 162.8, 162.4, 160.7, 139.4, 137.1, 135.8, 114.8, 114.3, 114.2, 113.7, 97.6, 73.6, 73.1, 72.7, 68.1, 67.5, 51.6, 47.4, 38.9, 38.6, 29.6, 28.6, 25.0, 22.6, 22.4, 20.2, 17.3, 16.9. HRMS (ESI) calcd for C\(_{61}\)H\(_{93}\)N\(_3\)Na\(_2\)O\(_{15}\). ([M+2Na]\(^{+}\)) 1153.6402, found 1153.6426.

**Compound 5.** \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) 10.19 (s, 2H), 10.15 (s, 2H), 10.11 (s, 2H), 8.45 (s, 2H), 8.40 (s, 1H), 8.36 (br, 3H), 8.21 (s, 2H), 7.83 (s, 2H), 7.73 (s, 2H), 7.71 (s, 2H), 6.97 (s, 2H), 4.36-4.30 (m, 8H), 3.97 (br, 4H), 3.53-3.50 (m, 4H), 3.48-3.45 (m, 4H), 3.06 (t, \(J = 16\) Hz, 6H), 1.87-1.83 (m, 3H), 1.52-1.47 (m, 4H), 1.30-1.21 (m, 20H), 0.92-0.89 (m, 18H), 0.70-0.67 (m, 24H); \(^{13}\)C NMR (75 MHz, DMSO-d\(_6\)) \(\delta\) 168.4, 166.5, 166.3, 162.6, 160.0, 139.5, 138.8, 138.7, 136.4, 136.4, 134.2, 115.8, 115.7, 114.0, 113.6, 113.2, 98.8, 72.6, 66.5, 46.7, 38.3, 28.1, 24.4, 23.9, 22.3, 22.3, 20.2, 16.8; MS (MALDI-TOF) \(m/z\), Calcd for C\(_{85}\)H\(_{123}\)N\(_9\)O\(_{17}\) 1541.90 (M\(^+\)), Found 1564.9 (M+Na\(^+\)).
II. GPC Data of 3a, 3b and 3c

**GPC measurements.** GPC measurements on the three fractions of 3 were performed with a GMH<sub>HR</sub>-N column, with a flow rate of 0.35 ml/min, and using THF as the eluting solvent at room temperature. The injection volume was 10 µL and UV detection at 254 nm was applied. Molecular weights and molecular-weight dispersity were calculated based on 12 polystyrene standards (M<sub>w</sub> = 500 to 1.11×10<sup>6</sup>, Table S1).

**Table S1.** The molecular weights of the 12 polystyrene standards (polydispersity <1.1)

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**GPC traces and results of 3a**
GPC traces and results of 3b

![Graph showing GPC traces and results]

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**GPC traces and results of 3c**

![GPC Graph]

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**GPC Summary**

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III. 1D $^1$H and $^{13}$C NMR Spectra

$^1$H NMR spectrum of 4

$^{13}$C NMR spectrum of 4
$^1$H NMR spectrum of 5

$^{13}$C NMR spectrum of 5
V. Concentration-Dependent $^1\text{H}$ NMR Spectra of 3a, 3b, 3c and 4

![Chemical structure](image)

Concentration-Dependent $^1\text{H}$ NMR Spectra of 3a

3a: $n=56$
3b: $n=30$
3c: $n=16$
Concentration-Dependent 1H NMR Spectra of 3b

Concentration-Dependent 1H NMR Spectra of 3c
Concentration-Dependent 1H NMR Spectra of 4

VI. UV Data of 3a, 3b, 3c and 4

UV Spectra of 3a (in CHCl₃)
UV Spectra of 3b (in CHCl₃)

UV Spectra of 3c (in CHCl₃)
UV Spectra of 4 (in CHCl₃)
VII. Additional CD Spectra

The CD Spectra of 4 (in CHCl₃)
The CD spectra of 5 (10 µM in CHCl₃) at -10 °C and 60 °C
Temperature-dependent CD Spectra of 3a (70 μM, CHCl₃)
The CD Spectrum of 3a in THF (20 µM, room temperature)