

Synthesis of Fully Soluble Azomethine-Bridged Ladder-Type Poly(*p*-phenylenes) by Bischler–Napieralski Reaction

Yulan Chen, Weiguo Huang, Cuihong Li, and Zhishan Bo*

Institute of Polymer Chemistry and Physics, College of Chemistry, Beijing Normal University, Beijing 100875, China

Received September 14, 2010

Revised Manuscript Received November 20, 2010

Introduction. In recent years, ladder-type conjugated polymers have attracted tremendous scientific attention.¹ The rigid and planar main chain structures of ladder-type conjugated polymers endow them with attractive physical properties such as high carrier mobility and luminescence intensity.² Exploration of structurally defined conjugated ladder-type polymers is thus highly required, owing to their potential applications such as optoelectronics, microelectronics, and chemical and biological sensors. During the past decade, great effort has been made in the synthesis of ladder polymers.³ However, synthesis of conjugated ladder polymers, especially soluble and structurally perfect heteroaromatic ladder polymers, remains a challenge. Although, Tour et al. have reported the synthesis of azomethine-bridged ladder polymers by Schiff base formation between alternating amine and ketone functional groups. However, the known ladder polymers synthesized by Schiff base formation reactions were only soluble in acidic media such as CH_2Cl_2/TFA (3/2), usually insoluble in normal organic solvents.^{3c}

In previous work, we have reported a facile synthesis of 3,8-dibromo-substituted phenanthridine derivatives by Bischler–Napieralski cyclization.⁴ A set of 4,4'-dibromo-2acylbiphenyls cyclized to 3,8-dibromophenanthridine monomers with nearly quantitative yields (Scheme 1). Herein, we apply this reaction to the synthesis of azomethine-bridged ladder-type poly(*p*-phenylene)s. A new kind of poly(laddertype phenanthridine)s with good structural perfection has been readily synthesized. To the best of our knowledge, this is the first report on synthesis of fully soluble azomethinebridged ladder-type conjugated polymers. Preliminary photophysical property studies illustrated that this kind of laddertype polymer is a promising chemosensor material.

Experimental Section. *Materials.* Unless otherwise noted, all chemicals were purchased from commercial suppliers and used without further purification. Phosphoryl trichloride was freshly distilled before use. Tetrahydrofuran (THF) was distilled over sodium and benzophenone. Triethylamine (TEA) was distilled over CaH₂ before use. All reactions were performed under an atmosphere of nitrogen and monitored by thin layer chromatography (TLC) with silica gel 60 F254 (Merck, 0.2 mm). Column chromatography was carried out on silica gel (200–300 mesh). The catalyst precursor Pd(PPh₃)₄ was prepared according to the literature⁵ and stored in a Schlenk tube under nitrogen. 2,7-Dibromo-9*H*-carbazole⁶ and 9,9-dioctylfluorene-2,7-diboronic pinacol ester⁷ were prepared according to literature procedures.

Characterization. ¹H and ¹³C NMR spectra were recorded on a Bruker AV400 or an AV600 spectrometer. Gel permeation chromatography (GPC) measurements were performed on Waters 410 system against polystyrene standards with THF as an eluent. UV-vis absorption spectra were obtained on a Shimadzu UV-vis spectrophotometer model UV-1601 PC. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Absolute fluorescence quantum yields of polymers were measured on a Fluoromax-4 fluorescence spectrophotometer. Elemental analyses were performed on a Flash EA 1112 analyzer. Fourier transform infrared (FT-IR) spectra were measured at room temperature using a Bruker Tensor 27 FT-IR spectrometer.

2,7-Dibromo-9-dodecyl-9H-carbazole (2). 60 wt % NaH (0.96 g, 24 mmol) and 1-bromododecane (3.26 g, 13.1 mmol) were added into the solution of 2,7-dibromo-9H-carbazole, 1 (3.27 g, 10.1 mmol), in DMF (40 mL). The mixture was stirred overnight at room temperature. Then the mixture was poured into water (200 mL), the aqueous layer was extracted with diethyl ether (2 \times 40 mL), and the combined organic layers were dried over Na₂SO₄ and evaporated to dryness. The crude product was purified by chromatography on silica gel eluting with petroleum ether to afford 2 as a colorless solid (4.9 g, 99%). ¹H NMR (CDCl₃, 600 MHz): δ 7.75 (d, 2H, ArH), 7.41 (s, 2H, ArH), 7.22 (d, 2H, ArH), 4.04 (t, 2H, CH₂), 1.71 (m, 2H, CH₂), 1.26-1.15 (m, 18H, CH₂), 0.79 (t, 3H, CH₃). ¹³C NMR (CDCl₃, 150 MHz): δ 141.34, 122.51, 121.45, 121.26, 119.69, 111.99, 43.32, 31.94, 29.59, 29.51, 29.35, 28.77, 27.18, 22.72, 14.16. Anal. Calcd for C₂₄H₃₁Br₂N: C, 58.43; H, 6.33; N, 2.84. Found: C, 58.43; H, 6.24; N, 2.77.

2,7-*Dibromo-3,6-dinitro-9-dodecyl-9H-carbazole* (**3**). A mixture of **2** (7.4 g, 15.0 mmol), acetic acid (200 mL), and concentrated nitric acid (40 mL) was heated to reflux overnight. After cooling, the precipitate was collected by filtration, and the crude product was recrystallized from ethanol and dried under high vacuum to afford **3** as a slight yellow solid (5.4 g, 62%). ¹H NMR (CDCl₃, 600 MHz): δ 8.59 (s, 2H, ArH), 7.65 (s, 2H, ArH), 4.20 (t, 2H, CH₂), 1.78 (m, 2H, CH₂), 1.26–1.13 (m, 18H, CH₂), 0.76 (t, 3H, CH₃). ¹³C NMR (CDCl₃, 150 MHz): δ 143.32, 143.13, 120.96, 119.51, 115.68, 113.90, 44.29, 31.88, 29.57, 29.51, 29.41, 29.30, 29.20, 28.79, 27.06, 22.67, 14.11. Anal. Calcd for C₂₄H₂₉Br₂N₃O₄: C, 49.42; H, 5.01; N, 7.20. Found: C, 49.45; H, 5.11; N, 6.89.

3,6-Bis(dodecanamido)-2,7-dibromo-9-dodecyl-9H-carbazole (5). To a solution of 3 (5.0 g, 8.6 mmol) in 200 mL of acetic acid was added aqueous HCl (45 mL, 32%). Tin powder (10.0 g, 84.0 mmol) was then added portionwise over 10 min, and the reaction mixture was heated to reflux overnight. After cooling, the mixture was poured into ice water (400 mL) and then neutralized with aqueous NaOH solution (20%) until the pH was 7. The precipitate was collected by filtration and dried under high vacuum to give the crude product 4 as a vellow solid. Because of the relative instability of the diamine 4 in air, the crude product of 4 was used for next step without further purification. ¹H NMR (CDCl₃, 400 MHz): δ 7.99 (s, br, 2H, NH), 7.40 (s, 2H, ArH), 7.34 (s, 2H, ArH), 3.92 (t, 2H, CH₂), 2.01 (m, 2H, CH₂), 1.26–1.21 (m, 18H, CH₂), 0.86 (t, 3H, CH₃). To a dry THF solution (30 mL) of 4 and triethylamine (15 mL) was added dropwise a dry THF solution (35 mL) of dodecanoyl chloride (8.0 g, 36.5 mmol) at 0 °C. After stirring at room temperature for 24 h, the solution was poured into water (80 mL) and the aqueous solution was extracted with diethyl ether $(2 \times 50 \text{ mL})$. The combined

^{*}Corresponding author. E-mail: zsbo@bnu.edu.cn.

organic extracts were dried over anhydrous Na₂SO₄ and evaporated to dryness. The residue was purified by chromatography on silica gel eluting with CH₂Cl₂ and recrystallization from CH₂Cl₂/*n*-Hex to afford **5** as a colorless solid (1.75 g, 23%). ¹H NMR (CDCl₃, 600 MHz): δ 8.54 (s, 2H, NH), 7.49 (s, 2H, ArH), 7.30 (s, 2H, ArH), 3.94 (t, 2H, CH₂), 2.37 (t, 4H, CH₂), 1.70 (m, 8H, CH₂), 1.34–1.13 (m, 48H, CH₂), 0.77 (t, 9H, CH₃). ¹³C NMR (CDCl₃, 150 MHz): δ 171.45, 138.29, 127.33, 122.07, 115.87, 114.05, 112.00, 43.28, 37.74, 31.92, 29.63, 29.60, 29.55, 29.48, 29.45, 29.33, 28.75, 27.11, 25.81, 22.69, 14.12. Anal. Calcd for C₄₈H₇₇Br₂N₃O₂: C, 64.93; H, 8.74; N, 4.73. Found: C, 64.00; H, 8.44; N, 4.60. ESI⁺ HRMS: calcd for C₄₈H₇₇Br₂N₃O₂ 885.43825; found 886.44494 [M + H]⁺.

Polymer P1. A mixture of 5 (0.10 g, 0.11 mmol), 9,9-dioctylfluorene-2,7-diboronic pinacol ester (0.073 g, 0.11 mmol), NaHCO3 (0.38 g, 4.5 mmol), THF (12 mL), toluene (4 mL), and H₂O (6 mL) was carefully degassed before and after $Pd(PPh_3)_4$ (1.3 mg, 1.1 μ mol) was added. The mixture was heated to reflux and stirred under nitrogen for 96 h. The reaction mixture was extracted with $CHCl_3$ (3 × 30 mL), and the combined organic layers were dried over anhydrous Na₂SO₄. After the removal of most of solvent, the residue was precipitated into methanol. The resulted precipitate was collected by filtration and dried under vacuum to give P1 as a grayish solid (0.096 g, 76%). ¹H NMR (CDCl₃, 400 MHz): δ 8.90 (broad, 2H), 7.92 (broad, 2H), 7.53 (broad, 4H), 7.34 (broad, 2H), 7.18 (broad, 2H), 4.30 (broad, 2H), 2.24 (broad, 4H), 2.09 (broad, 2H), 1.91 (broad, 2H), 1.70 (m, 4H), 1.63 (broad, 2H), 1.44-1.14 (m, 77H), 0.88 (broad, 6H), 0.82 (broad, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 171.17, 151.53, 140.12, 138.67, 132.97, 128.76, 126.83, 124.22, 122.53, 120.31, 115.80, 109.89, 55.49, 40.36, 37.63, 31.92, 31.81, 30.22, 29.68, 29.64, 29.54, 29.42, 29.36, 29.21, 29.17, 29.12, 27.40, 25.77, 22.69, 22.64, 14.12, 14.06.

Scheme 1. Facile Synthesis of 3,8-Dibromophenanthridine Derivatives by Bischler-Napieralski Cyclization



Polymer **P2**. A solution of **P1** (0.059 g) and P_2O_5 (1 g) in freshly distilled POCl₃ (12 mL) was stirred at reflux for 30 h under N₂. The solvent was removed under high vacuum, the residue was diluted with ethyl acetate (15 mL), and water (30 mL) was added slowly. The aqueous layer was adjusted to pH = 10 with NaOH solution (5 M) and then extracted with CHCl₃ (2×20 mL). The combined organic layers were dried over anhydrous Na₂SO₄. After the removal of most of solvent, the residue was precipitated into methanol. The resulted precipitate was collected by filtration and dried under high vacuum to give P2 as a brown solid (0.045 g, 79%). ¹H NMR (CDCl₃, 400 MHz): δ 9.11 (broad, 2H), 8.82 (broad, 4H), 8.55 (broad, 2H), 4.82 (broad, 2H), 3.65 (broad, 4H), 2.58 (broad, 2H), 2.32 (broad, 2H), 2.24 (m, 4H), 1.70 (broad, 2H), 1.44–1.12 (m, 77H), 0.88 (broad, 12H). ¹³C NMR (CDCl₃, 100 MHz): & 38.36, 38.31, 38.00, 33.67, 32.83, 31.06, 30.94, 30.71, 30.60, 30.56, 30.33, 30.26, 30.12, 27.99, 25.37, 23.59, 20.63, 15.01.

Results and Discussion. The synthetic route leading to azomethine-bridged ladder-type poly(p-phenylene)s is shown in Scheme 2. 3.6-Bis(dodecanamido)-2,7-dibromo-9-dodecyl-9H-carbazole is the key monomer, whose synthesis is rather straightforward. Starting from 2,7-dibromo-9H-carbazole, its reaction with 1-bromododecane under NaH/DMF conditions gave 2,7-dibromo-9-dodecyl-9H-carbazole 2 in a yield of 99%. Nitration of 2 with a mixture of concentrated nitric acid and acetic acid under reflux conditions afforded 2,7-dibromo-3,6-dinitro-9-dodecyl-9H-carbazole 3 in a 62% yield. Subsequent reduction of the nitro groups with Sn/H⁺ furnished the corresponding diamine 4. Diamine 4 is not very stable in air, so the crude 4 was used for the next step without further purification. The reaction of 4 with dodecanoyl chloride in a solvent mixture of THF and TEA furnished 3,6bis(dodecanamido)-2,7-dibromo-9-dodecyl-9H-carbazole (5) in a total yield of 23%. Except for compound 4, all other intermediates were unambiguously characterized by ¹H and ¹³C NMR spectroscopy, elemental analysis, or high-resolution mass spectroscopy.

The synthesis of azomethine-bridged ladder-type poly-(*p*-phenylene)s involves two key steps: (1) Suzuki–Miyaura– Schlüter polycondensation (SMSPC) was used to prepare the single-chain carbazole-*alt*-fluorene polymer **P1** bearing lateral dodecanamide chains on each carbazole repeating unit,



Scheme 2. Synthetic Route to Azomethine-Bridged Ladder-Type Poly(p-phenylene)s



Figure 1. ¹H NMR spectra of single-stranded polymer P1 and ladder polymer P2 in aromatic region.

and (2) Bischler-Napieralski cyclization was used to achieve azomethine-bridged ladder-type poly(p-phenylene)s P2. SMSPC of dibromo monomer 5 and 9,9-dioctylfluorene-2,7-diboronic pinacol ester 6 was carried out in a biphasic mixture of THF and aqueous NaHCO₃ solution with $Pd(PPh_3)_4$ as the catalyst precursor afforded P1 in a yield of 76%. The single-stranded polymer P1 was converted to the corresponding azomethine-bridged double-stranded laddertype poly(p-phenylene)s P2 in a yield of 79% under the optimized Bischler-Napieralski reaction conditions, using $POCl_3$ as the solvent and P_2O_5 as the catalyst at refluxing condition. With five lateral long alkyl chains on each repeating unit, both the single-stranded polymer P1 and the laddertype polymer **P2** are readily soluble in common organic solvents such as chloroform and THF, making the characterization of their structures very convenient. ¹H and ¹³C NMR spectra of the two polymers P1 and P2 confirmed the expected structures.

The molecular weights of two polymers were measured by gel permeation chromatography (GPC) against polystyrene standards with THF as an eluent. The number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of **P1** are 20.0 and 32.0 kDa, respectively, whereas after ring closure M_n and M_w of ladder-type polymer **P2** decreased to 16.0 and 23.0 kDa, respectively. GPC is known not to be a good method to determine the actual molecular weight of rodlike polymers, and the molecular weights determined by GPC are only a relative measurement of the hydrodynamic volume of polymers. The difference in the elution curves also maybe due to the different interaction with the column material.

In our previous paper, we have proved that Bischler-Napieralski cyclization is a very effective route to prepare phenanthridine derivatives, and in many cases quantitative yield can be achieved.' To verify that the polymer-based analogous ring closure reaction also goes to completion, ¹H NMR and FT-IR spectroscopy investigations have been carried out. The assigned ¹H NMR spectra of the single-stranded polymer P1 and the ladder-type polymer P2 are shown in Figure 1 for a comparison. In the aromatic region, the singlestranded polymer P1 shows five broad signals peaked at 8.90, 7.92, 7.53, 7.34, and 7.18 ppm, whereas the ladder-type polymer P2 shows only three broad peaks peaked at 9.09, 8.80, and 8.51 ppm. In the ¹³C NMR spectrum of P2, the disappearance of the carbonyl signal also indicates that the ring closure reaction is complete. The FT-IR spectra of the single-stranded precursor polymer P1 and the laddertype polymer P2 are shown in Figure 2 for a comparison.



Figure 2. FT-IR spectra of the polymers P1 and P2.

In the FT-IR spectrum of the single-stranded polymer P1, the sharp absorption peak at 3423 cm^{-1} is due to the stretching mode of the free NH of amido groups, the broad absorption peak at 3269 cm^{-1} is due to the stretching mode of the hydrogen bonding NH of amide groups, and the absorption peaks at $1689 \text{ and } 1663 \text{ cm}^{-1}$ are the corresponding the C=O stretching vibrations of the free and hydrogen-bonding amido groups, respectively. In the FT-IR spectrum of the ladder-type polymer P2, the characteristic absorptions related to amido groups disappeared completely, indicating that a complete cyclization has been achieved.

Photophysical properties of single-stranded polymer P1 and double-stranded polymer P2 in THF and chloroform solutions and films were investigated by UV-vis absorption and photoluminescent (PL) spectroscopy. It is worth to note that the ladder-type polymer P2 has an alternating donoracceptor structure in the polymer main chain. The normalized UV-vis absorption and photoluminescent (PL) spectra of single-stranded polymer P1 and P2 in dilute THF solutions are shown in Figure 3a. P1 exhibited a strong featureless absorption in the ultraviolet region ranging from 320 to 410 nm with a maximum at 355 nm and a broad featureless emission band peaked at 441 nm. Ladder polymer P2 showed well-resolved strong absorption in the ultraviolet region ranging from 300 to 450 nm with three peaks at 391, 403, and 416 nm and two shoulders at 365 and 428 nm, indicating the existence of a highly defined electronic structure that is low in defects.^{1b} P2 displayed a well-resolved PL spectrum with the emission maximum at 496 nm and a shoulder at about 470 nm. Molar absorption coefficients of P1 and P2 are 69117 and 12524, respectively. Compared with the single-stranded polymer P1, significant bathochromic shifting of the absorption and emission spectra of ladder polymer **P2** has been found, which suggests that the effective conjugation length has been extended after the polymer was transformed to ladder structure. The normalized UV-vis absorption and PL spectra of P1 and P2 in chloroform solutions are shown in Figure 3b. The absorption and emission spectra of P1 in chloroform solution are quite similar to those in THF solution. In chloroform solution, the ladder-type polymer P2 displayed a broad absorption in the range 300-450 nm with three peaks at 368, 391, and 416 nm and a shoulder at 432 nm. In chloroform solution, P2 showed a broad emission band in the range 400-600 nm with three peaks located at 432, 464, and 493 nm. In comparison with the emission spectrum in THF solution, the emission spectrum of P2 in chloroform solution is much broader and slightly hypsochromically shifted. The above results illustrated



Figure 3. Normalized UV absorption and photoluminescent spectra of P1 and P2 in THF solutions (a), CHCl₃ solutions (b), and films (c).

that **P2** has less intramolecular interaction between donor and acceptor units in the ground state, whereas the emission spectra of **P2** displayed remarkable solvent dependence behaviors. The absolute quantum efficiencies in highly dilute THF and chloroform solutions are 30% and 24% for **P1** and 11% and 10% for **P2**, respectively. The normalized UV-vis absorption and emission spectra of **P1** and **P2** in films are shown in Figure 3c. Compared to its behaviors in solution, the absorption and emission spectra of **P1** were only slightly bathochromically shifted. For ladder polymer **P2**, both the absorption and emission spectra became featureless and bathochromically shifted for 32 and 107 nm, respectively. This result indicated that the planar ladder polymer **P2** formed aggregation in solid films.

The nitrogen atom on the ladder polymer backbone can be easily protonated and deprotonated.^{3e,8} The protonation



Figure 4. (a) UV-vis absorption spectra of P2 in THF (6×10^{-6} M for repeating units) at various concentration of TFA: [TFA] = 0, 8×10^{-7} , 8×10^{-6} , 8×10^{-5} , 8×10^{-4} , 8×10^{-3} , 1.2×10^{-2} , 1.6×10^{-2} , 4.8×10^{-2} , 3.2×10^{-1} M. (b) PL spectra P2 in THF (6×10^{-6} M for repeating units) at various concentration of TFA: [TFA] = 0, 8×10^{-7} , 8×10^{-6} , 8×10^{-5} , 8×10^{-3} , 1.2×10^{-2} , 1.6×10^{-7} , 8×10^{-6} , 8×10^{-5} , 8×10^{-4} , 8×10^{-3} , 1.2×10^{-2} , 1.6×10^{-2} , 4.8×10^{-2} , 3.2×10^{-1} M and the neutralization with TEA. The excitation wavelength is 391 nm.

and deprotonation processes are reversible. The UV-vis absorption spectra of ladder polymer P2 by titration with trifluoroacetic acid (TFA) are shown in Figure 4a. With the addition of TFA to a solution of **P2** in THF (6×10^{-6} M), the absorption spectrum of the protonated ladder polymer became broader, red-shifted, and featureless with the absorption maximum located at 410 nm. For the emission spectra, the intensity of peaks at 470 and 296 nm decreased with the addition of TFA, and a new featureless weak green emission band peaking at 545 nm appeared gradually with the disappearance of the two blue emission peaks. The protonated ladder polymer can be easily deprotonated by the addition of triethylamine (TEA). After the addition of a droplet of TEA to the protonated ladder polymer solution, the long wavelength green emission completely disappear with partial recovery of the blue emission. These preliminary optic property investigations revealed that azomethine-bridged ladder-type poly(*p*-phenylene)s are promising protic acid sensitive materials.

Conclusions. In conclusion, we have developed a facile approach to synthesize azomethine-bridged ladder-type poly(*p*-phenylene)s. The newly developed synthetic method allows the preparation of ladder polymers with good structural perfection. The ladder polymers we synthesized are of

high molecular weight and highly soluble in common organic solvents. Photophysical property studies indicated that the phenanthridine-containing ladder-type polymers are promising pH sensor materials.

Acknowledgment. Financial support by the NSF of China (Grants 20774099, 20834006, and 50821062), the 863 Program (Grant 2008AA05Z425), and the National Basic Research Program of China (973 Program: 2009CB623601) is gratefully acknowledged.

Supporting Information Available: Figures S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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