

Synthesis and characteristic of novel polyamides with bis(phenoxy)phenyl-2-amino-9,9-diphenylfluorene

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Abstract A series of polyamides 6a-6c with triphenylamine unites were prepared from a novel diamine, *N,N*-bis((4-amine) phenoxy)phenyl-2-amino-9,9-diphenylfluorene and three dicarboxylic acids via a condensation polymerization.

Keywords: Triphenylamine; Fluorene; Polyamide

Introduction

Polyamides are commercially important materials in a wide range of high technology applications. However, rigidity of backbone and strong interchain interactions result in high melting or glass-transition temperature which are limited their application fields [1]. The typical approaches to overcome the disadvantages include the introduction of flexible linkages, kinked or unsymmetrical structures, bulky packing-disruptive unites, and bulky lateral groups into the polymer backbone [2]. Triphenylamine with propeller starburst structure is well-known for the strong electron donating and excellent hole-transmission capability [3]. In particular, triphenylamine derivatives could switch their colors reversibly and stably during the oxidation-reduction process as long as the para-position of triphenylamine is protected effectively [4]. Thus, triphenylamine-containing materials are promising as an attractive family of electrochromic materials [5].

Herein, we synthesized a novel diamine, *N,N*-bis((4-amine) phenoxy) phenyl -2-amino-9,9-diphenylfluorene and derived polyamides were prepared via a condensation polymerization from the new diamine and dicarboxylic acids.

Experiment

Materials

2-amino-9,9-diphenylfluorene (TCI), 4-iodoanisole (Acros), 18-crown-6 (Acros), copper (Cu, Acros), Boron tribromide (BBr₃, Acros), 4-fluoronitrobenzene (Acros), 10% palladium on charcoal (Pd/C, TCI), hydrazine monohydrate (TCI), triphenyl phosphite (TPP, Acros) were used as received. 4,4'-dicarboxydiphenyl ether (5a, TCI), 2,2-bis(4-carboxyphenyl)hexafluoropropane (5b, TCI) and trans-1,4-cyclohexanedicarboxylic acid (5c, TCI) were dried under vacuum at 100 °C for 10 h prior to use. Potassium carbonate and calcium chloride were dried in vacuum at 180 °C for 12 h prior to use. O-dichlorobenzene, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and dichloromethane (CH₂Cl₂) were dried over 4 Å molecular sieves prior to use. The other commercially reagents and solvents were used without further purification.

Synthesis of monomers

N,N-di(4-methoxyphenyl)-2-amino-9,9-dimethylfluorene (1)

In a 250 mL round-bottom flask equipped with a stirring bar under nitrogen atmosphere, a mixture of 15.0 g (45.0 mmol) of 2-amino-9,9-diphenylfluorene, 26.2 g (112.5 mmol) of 4-iodoanisole, 7.2 g (112.5 mmol) of copper, 15.6 g (112.5 mmol) of potassium carbonate and 3.0 g (11.2 mmol) of

18-crown-6 in 60 mL dried *o*-dichlorobenzene was heated with stirring at 175 °C for 20 h. The reaction mixture was hot filtered, and the filtrate was poured into 500 mL of stirred ethanol slowly. The precipitated product was collected by filtration and then recrystallized from toluene/*n*-hexane to afford beige crystals 14.1 g in 57.4% yield with a melting point of 165 °C. IR (KBr): 2927 cm⁻¹, 2835 cm⁻¹ (-OCH₃, -CH stretch). ¹H NMR (300 MHz, δ, DMSO-*d*₆, ppm) 7.74 (d, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.28 – 7.15 (m, 7H), 7.06 – 6.99 (m, 4H), 6.97 (d, *J* = 9.0 Hz, 4H), 6.90 – 6.81 (m, 5H), 6.76 (dd, *J* = 8.3, 2.2 Hz, 1H), 3.72 (s, 6H).

N,N-di(4-hydroxyphenyl)-2-amino-9,9-dimethylfluorene (2)

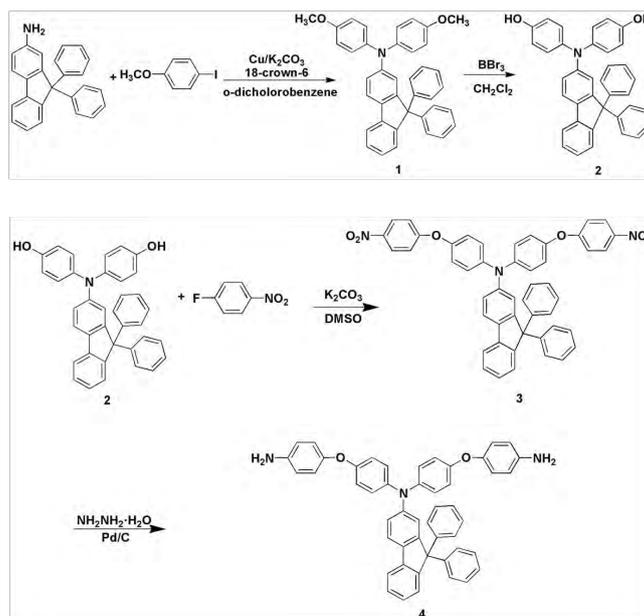
A mechanically stirred solution of 12.0 g (22.0 mmol) of compound 1 in 160 mL dry dichloromethane was cooled to -25 °C, and then 88.0 mL (88.0 mmol, 1 M solution in CH₂Cl₂) of BBr₃ was added drop wise under nitrogen atmosphere. After stirring for 1 h at this temperature, the reaction mixture was allowed to warm to 0 °C and stirred for 6 h. Quenched the reaction by adding methanol carefully at -25 °C, and the reaction solution was stirred for 1 h at room temperature. The solution was poured into 1 L stirred saturated aqueous solution of NaHCO₃ slowly to form green precipitate, the precipitate was collected by filtration, washed by water at least three times and dried under vacuum to afford green powder 9.3 g in 81.7% yield. IR (KBr): 3313 cm⁻¹ (-OH stretch). ¹H NMR (300 MHz, δ, DMSO-*d*₆, ppm) 9.31 (s, 2H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.28 – 7.13 (m, 7H), 7.07 – 6.97 (m, 4H), 6.88 (d, *J* = 8.8 Hz, 4H), 6.77 (d, *J* = 2.2 Hz, 1H), 6.74 – 6.62 (m, 5H).

N,N-bis((4-nitro)phenoxy)phenyl-2-amino-9,9-diphenylfluorene (3)

In a 250 mL round-bottom flask with a stirring bar, a mixture of 8.0 g (15.4 mmol) of dihydroxy compound 2, 5.0 g (35.4 mmol) of 4-fluoronitrobenzene and 4.9 g (35.4 mmol) of potassium carbonate in 60 mL of dried DMSO was heated with stirring at 120 °C for 12 h under nitrogen atmosphere. After cooling to the room temperature, the mixture was poured into 500 mL of stirred ethanol slowly to form yellow precipitate which was collected by filtration and washed by hot water. Then the crude product was recrystallized from DMF/ethanol, yielding 9.2 g desired dinitro compound 3 in 78.3% with a melting point of 234 °C. IR (KBr): 1590 cm⁻¹, 1345cm⁻¹ (-NO₂ stretch). ¹H NMR (300 MHz, δ, DMSO-*d*₆, ppm) 8.26 (d, *J* = 9.2 Hz, 4H), 7.92 – 7.81 (m, 2H), 7.42 (d, *J* = 7.1 Hz, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.31 – 7.19 (m, 7H), 7.19 – 7.11 (m, 12H), 7.10 – 7.04 (m, 6H).

N,N-bis((4-amino)phenoxy)phenyl-2-amino-9,9-diphenylfluorene (4)

In a 250 mL round-bottom flask with a stirring bar, 8.0 g (10.5 mmol) of dinitro compound 3 and 1.0 g of 10% Pd/C were dissolved in 20 mL ethanol and 40 mL 1,4-dioxane under nitrogen atmosphere. Then the solution was heated to reflux, and 15 mL of hydrazine monohydrate was added slowly to the mixture. After a further 12h of reflux, the solution was filtered hot to remove Pd/C, and the filtrate was cooled under nitrogen flow to precipitate white product. The product was collected by filtration and dried under vacuum to obtain 6.2 g of diamine in 84.1% yield with a melting point of 133 °C. IR (KBr): 3465cm⁻¹, 3370cm⁻¹ (-NH₂ stretch). ¹H NMR (300 MHz, δ, DMSO-*d*₆, ppm) 7.77 (d, *J* = 7.6 Hz, 1H, H_h), 7.73 (d, *J* = 8.8 Hz, 1H, H_g), 7.38 (d, *J* = 7.2 Hz, 1H, H_k), 7.34 (d, *J* = 7.4 Hz, 1H, H_i), 7.27 – 7.17 (m, 7H, H_m+H_n+H_j), 7.07 – 6.99 (m, 4H, H_l), 6.96 (d, *J* = 8.9 Hz, 4H, H_b), 6.87 (s, 1H, H_e), 6.84 (d, *J* = 2.1 Hz, 1H, H_f), 6.79 (d, *J* = 3.0 Hz, 4H, H_a), 6.76 (d, *J* = 2.8 Hz, 4H, H_c), 6.59 (d, *J* = 8.8 Hz, 4H, H_a), 4.97 (s, 4H, NH₂).



Scheme 1 Synthetic route to the diamine 4.

Synthesis of polyamides

The synthesis of 6a was used as an example to illustrate the general synthetic route used to produce the polyamides. In a 50 mL three-neck round-bottom flask under nitrogen atmosphere, a mixture of 0.6998 g (1 mmol) of diamine 4, 0.2582 g (1 mmol) of 4,4'-dicarboxydiphenyl ether (5a), 0.15 g of dried calcium chloride, 1 mL of triphenyl phosphite, 0.5 mL pyridine and 2.5 mL NMP. The reaction mixture was heated with stirring at 120 °C for 3 h. The resulting viscous polymer solution was poured slowly into 300 mL stirring methanol, producing a fiber-like precipitate that was collected by filtration, washed thoroughly by hot water and ethanol, and dried under vacuum at 100 °C. Reprecipitations of the polymer from DMAc into methanol were carried out twice for further purification. ¹H NMR (300 MHz, δ, DMSO-*d*₆, ppm): 10.29 (s, 2H, amide N-H), 8.07 (d, *J* = 8.4 Hz, 4H, H_o), 7.81 (m, 6H, H_a+H_g+H_h), 7.51 – 7.30 (m, 2H, H_k+H_i), 7.30 – 7.14 (m, 11H, H_p+H_m+H_n+H_j), 7.13 – 6.84 (m, 18H, H_d+H_l+H_b+H_c+H_e+H_f).



Scheme 2 Synthesis of polyamides 6a-6c.

Measurements

Fourier transform infrared (FTIR) spectra were recorded through a Burkert Vector 22 spectrometer at a resolution of 4 cm^{-1} in the range of 400-4000 cm^{-1} . Nuclear magnetic resonance (NMR) spectra were determined on a BRUKER-300 spectrometer at 300MHz for ^1H NMR in deuterated DMSO.

Results and Discussion

Monomer synthesis

As depicted in scheme 1, the new diamine, *N,N*-bis((4-amine) phenoxy)phenyl-2-amine-9,9-diphenylfluorene was successfully synthesized by a four-step reaction starting from 2-amino-9,9-diphenylfluorene and 4-iodoanisole. The compound 1 *N,N*-di(4-methoxyphenyl)-2-amino-9,9-dimethylfluorene was synthesized via Ullmann reaction. The intermediate dihydroxy compound 2 was prepared by the demethylation of the dimethoxy compound 1 with boron tribromide. The target diamine monomer 4 was synthesized by Pd/C-catalyzed reduction of the dinitro compound 3 resulting from nucleophilic aromatic fluoro-displacement reaction of dihydroxy compound 2 with *p*-fluoronitrobenzene in the presence of K_2CO_3 . FTIR and NMR spectroscopic techniques were used to identify the structures of the compounds 1-4. Figure 1 illustrates ^1H NMR spectrum of target diamine 4. Assignments of each proton are also given in this figure and the NMR spectrum agrees well with the proposed molecular structure, which suggests that the target monomer 4 has been prepared successfully.

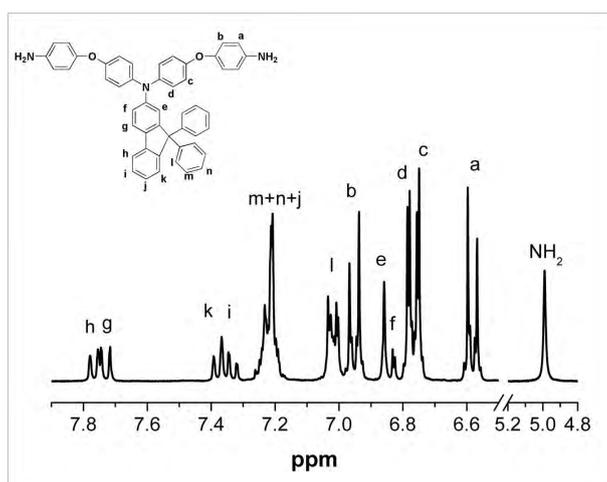


Fig. 1 ^1H NMR spectrum of diamine 4 in DMSO-d_6 .

Polymer synthesis

The three polyamides 6a-6c were prepared by a condensation polymerization from diamine 4 and three different dicarboxylic acids 5a-5c (scheme 2). All polymerization proceeded homogeneously and obtained viscous polymer solution, when pouring the polymer solution into stirred methanol, produce tough and fiber-like polymer precipitations. These precipitations were reprecipitate two times from DMAc into methanol for further purification. All these high molecular weights polyamides could be cast into flexible films. All the polyamides showed the characteristic absorption bands of amide at 1662 cm^{-1} and 3313 cm^{-1} (Fig. 2).

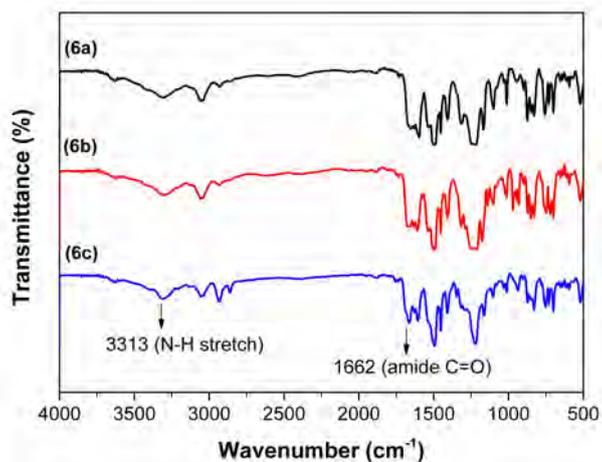


Fig. 2 FTIR spectra of polyamides 6a-6c.

Conclusion

In summary, a series of polyamides were synthesized via condensation polymerization reaction from a novel diamine, *N,N*-bis((4-amino)phenoxy)phenyl-2-amino-9,9-diphenylfluorene and three dicarboxylic acids.

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