

Synthesis, Characterization and Properties of Polymeric *p*-Benzoyl-4,4'-Diaminobenzoylaniline

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Abstract

An aromatic polyamide was synthesized by low-temperature poly-condensation reaction from terephthaloyl chloride and 4,4'-diaminobenzanilide (4,4'-DABA). The synthesized polyamide had a characteristic peak of carbon atoms in the amide group at 166 ppm, which was demonstrated by the solid nuclear magnetic resonance carbon spectrum. It was shown to be the stretching vibration absorption peak of the amide N-H bond at 3342 cm⁻¹ by Fourier infrared (FT-IR) spectroscopy. It was obtained that the energy band near 1100 - 1276 cm⁻¹ belongs to the absorption peak of the para-substituted benzene ring and the band near 2977 cm⁻¹ was the C-H stretching vibration peak of the benzene ring by Raman spectroscopy. The molecular structure of the synthesized polyamide compound was confirmed by FT-IR, Raman, and solid ¹³C-NMR spectroscopies. It was proved that the polymer is stable up to 300°C and has a relatively high stability by the thermogravimetric analysis. It was also confirmed by the fluorescence spectrum that it has a strong blue fluorescence near 420 nm. The morphological characteristics of the polymer were further demonstrated by electron scanning electron microscopy (SEM). The properties of polymeric *p*-benzoyl-4,4'-diaminobenzoyl-aniline were found to emit strong blue fluorescence and have good thermal stability, making it a promising functional material for fluorescence in the blue region with potential for large-scale applications.

Keywords

Aromatic Polyamide, Thermogravimetric Analysis, Heat Resistance, Polymeric *p*-Benzoyl-4,4'-Diaminobenzoylaniline

1. Introduction

Polyamide (PA), also known as nylon, is an important polymer with a repeated

amide group (-R-CO-NH-R'-) in the chain segment, and synthesized by a low-temperature poly-condensation reaction [1] [2] [3]. During the synthesis of polyamide, the raw material composition, crystallinity and molecular weight of the product could be changed by different processes to make a variety of products with different properties, such as engineering plastics and fibers [4].

With the expansion of polyamide applications to the high-end electronics industry and aviation industry, the heat resistance and mechanical properties of polyamides are put into higher demand by more demanding working environments [5]. Aliphatic polyamide chain segment has high amide bond density, easy-to-form hydrogen bond with water, strong water absorption, poor dimensional stability and thermal stability, which is difficult to apply to the above harsh environment. A new polyamide has been developed by Dupont Co. Ltd. with a large number of benzene rings in the main chain, and more than 85% of the amide groups are linked to benzene rings. This type of polyamide is called aromatic polyamide, which has extremely high strength, toughness and heat resistance, and plays an important role in aerospace, military and electronics and other cutting-edge industries [6].

In recent years, aromatic polyamides have been found by researchers to exhibit blue fluorescence under certain conditions [7]. Those blue fluorescence properties of the products are related to the polyamide in the benzene ring structures. In some studies, by introducing different groups or additives to the polyamide molecule, its molecular structure and electron density are altered, resulting in blue fluorescence under UV-vis excitation.

In addition, aromatic polyamides can also be combined with other substances to form complexes with new fluorescent properties in some cases. For example, by forming complexes with metal ions or alkali metal salts, aromatic polyamides may also exhibit blue fluorescence.

There are many methods to prepare polyamides, such as the high-pressure high-temperature solution poly-condensation method, low-temperature solution poly-condensation method, the polyester poly-condensation, interfacial polymerization method or the like, wherein the laboratory for high temperature and high-pressure reaction has a certain risk. The molecular weight of the polyester condensation product cannot be controlled and the molecular weight growth of the latter part of the reaction product is difficult. The interfacial polymerization method is difficult to recover solvents, with high solvent consumption and serious environmental pollution. The reaction conditions of the low-temperature solution poly-condensation method are simple. Post-treatment requires only cleaning and filter drying [8].

The polymeric *p*-benzoyl-4,4'-diaminobenzoylaniline compound synthesized in this paper was prepared by the low-temperature poly-condensation reaction, using terephthaloyl chloride and 4,4'-diaminobenzanilide (4,4'-DABA) as raw materials and referring to the method in literature [9]. The reaction device was dried in advance and N₂ seal was carried out to avoid side reactions and oxidation. The acyl chloride in terephthaloyl chloride is a highly reactive group, and a

large number of $-\text{CONH}-$ groups will be generated in the early stage of the reaction, causing the temperature of the system to rise rapidly so the reaction is carried out at low temperatures. CaCl_2 was chosen as the co-solvent because Ca^{2+} could complex with amide group in amide solvent, while free Cl^- could form hydrogen bonds with the hydrogen proton of polymer amide group, thus opening the hydrogen bond between polymer molecules, which was conducive to polymer dissolution [10]. The low-temperature poly-condensation method makes for a smooth reaction process with good heat exchange due to the fact that it is carried out in a solvent, and does not require much polymerization equipment.

In this paper, 4,4'-diaminobenzanilide and terephthaloyl chloride were condensed at low-temperature to obtain an aromatic polyamide. Its main advantages are high-temperature resistance, good thermal stability and fluorescence, which can be applied to some high-temperature resistant automotive parts and light-emitting diodes.

2. Experiments Details

2.1. Materials

All the solvents used in this synthesis were deoxidized by water removal before use. The water used in the laboratory is deionized water produced by the pure water equipment system. The reagent used in the experiment was anhydrous ethanol, which was purchased from Nanjing Chemical Reagent Co., LTD. *P*-benzoyl chloride, anhydrous calcium chloride CaCl_2 was purchased from Sinopharm Group Chemical Reagent Co., LTD. *P*-benzoyl chloride, 1-methyl-2-pyrrolidinone (NMP), purchased from Anhui Zesheng Technology Co., LTD.; 4,4'-diaminobenzanilide from Tixiai (Shanghai) Chemical Industry Development Co., LTD.

2.2. Preparation of Polymeric *p*-Benzoyl-4,4'-Diaminobenzoylaniline by Condensation at Low Temperature

The synthesis diagram is shown in **Figure 1**, and the specific steps are as follows:

Purging dinitrogen gas into a 250 mL three-port flask and drying the flask. Under the condition of heating, anhydrous calcium chloride (6.1 g, 55 mmol) and 1-methyl-2-pyrrolidinone (NMP) 100 mL were added in sequence. The complexation of solvent molecules with metal cations improved the solvation of the system and increased the solubility of 4,4'-diaminobenzanilide. Addition of 4,4'-diaminobenzanilide (1.14 g, 5 mmol) under dinitrogen atmosphere, stirring

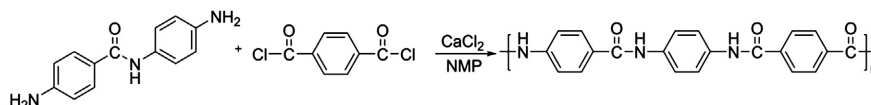


Figure 1. Schematic diagram of the synthesis of polymeric *p*-benzoyl-4,4'-diaminobenzoylaniline compounds.

fully at 60°C for about 30 min, to be completely dissolved, appearing in a pink solution. Cool down with an ice water bath, the temperature was controlled between 0°C - 5°C, addition of terephthaloyl chloride (1.01 g, 5 mmol) and stirring fully, appearing in a purple solution, reaction at low-temperature for 8 hours, continue to react at room temperature for 8 hours. After the reaction, the brown solution was poured into about 10 times deionized water to precipitate gray precipitation, stirred for about 1 hour, pumped and filtered under reduced pressure, washed with anhydrous ethanol (3 × 50 mL), and dried for 5 hours *in vacuo* at 120°C to obtain gray precipitated polymeric *p*-benzoyl-4,4'-diaminobenzoylaniline 2.02 g (93.9%).

2.3. Instruments

The solid ¹³C NMR was measured using a Bruker ALX 400 MHz nuclear magnetic resonance (NMR) spectrometer. The chemical shift (δ , ppm) was referenced to the standard substance SiMe₄. The infrared spectrum was obtained by using the KBr pellet method for sample preparation and measured on a Perkin-Elmer 16 PC FT-IR Fourier transform infrared spectrometer. The Raman spectrum was obtained by using a Renishaw inVia confocal Raman spectrometer. The UV-visible spectrum was measured by using a Shimadzu UV-2600 double-beam UV-visible spectrophotometer. The fluorescence spectrum was measured on a PerkinElmer LS-55 fluorescence spectrometer. The thermogravimetric curve data of the sample were obtained by using a Shimadzu DTG-60H instrument. The scan electron microscopy was performed by using a JEM-6480 scanning electron microscope with a tungsten filament.

3. Results and Discussion

3.1. Nuclear Magnetic Resonance (NMR) Carbon Spectrum Analysis

According to the solid ¹³C NMR spectrum as shown in **Figure 2**, the signal observed at the chemical shift 123 - 136 ppm is attributed to the characteristic peak of the carbon atom on the benzene ring, and the signal at 166 ppm is attributed to the characteristic peak of the middle carbon atom of the amide group, which mirrors the chemical shift of the characteristic peak of the polyamide unit in the literature [11].

3.2. Fourier Transform Infrared Spectroscopic Analysis

In the FT-IR spectrum of polymeric *p*-benzoyl-4,4'-diaminobenzoylaniline, the stretching vibration absorption peak of amide N-H bond is at 3342 cm⁻¹, the absorption peak of the C=O stretching vibration of the amide bond at 1658 cm⁻¹, which is the absorption band of amide I. It is bent by the N-H bending vibration in the amide group at 1515 cm⁻¹, which is the amide II absorption band. It is the bending vibration peak of the C-N bond at 720 cm⁻¹. By comparing the product with the raw material, it was found that the characteristic double peaks of

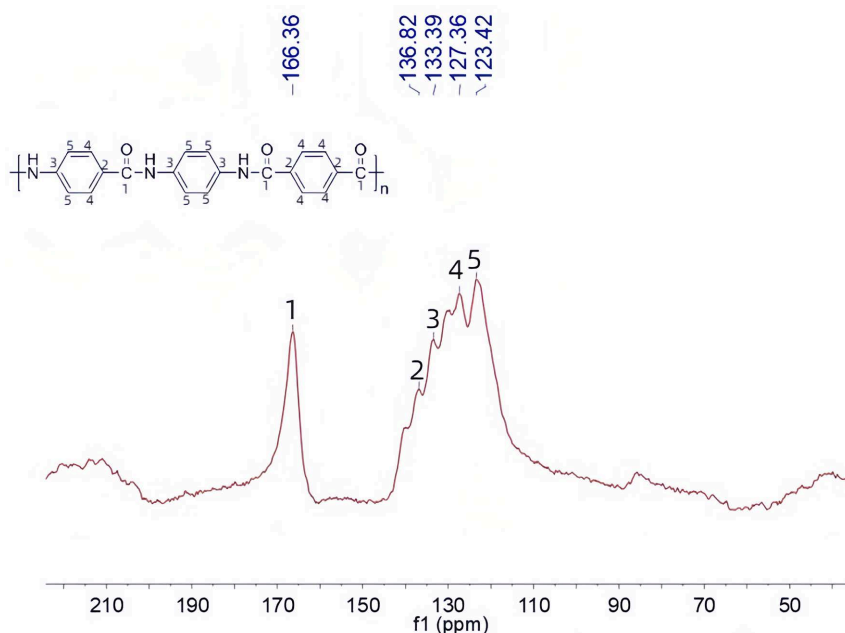


Figure 2. ^{13}C NMR spectrum of polymeric *p*-benzoyl-4,4'-diaminobenzoylaniline.

primary amine disappeared, and by comparing it with terephthaloyl chloride, it was found that the stretching vibration peak of terephthaloyl chloride C–Cl disappeared at about 856 cm^{-1} . The above analysis indicates that 4,4'-diaminobenzanilide reacted with terephthaloyl chloride to form polyamide, as shown in **Figure 3** below.

3.3. Raman Spectroscopic Analysis

As shown in **Figure 4**, comparing the Raman spectrum of terephthaloyl chloride and 4,4'-diaminobenzanilide, the characteristic absorption band of amide I band (stretching vibration of C=O bond) near 1604 cm^{-1} can be obviously observed on the spectra of polymeric *p*-benzoyl-4,4'-diaminobenzoylaniline. The band near $1100 - 1276\text{ cm}^{-1}$ belongs to the absorption peak of the *para*-substituted benzene ring, while the bands near 2977 and 3342 cm^{-1} are the stretching vibration absorption peak of the amide N–H bond and the C–H stretching vibration peak on the benzene ring, respectively. The reaction of 4,4'-diaminobenzanilide with terephthaloyl chloride to form polymeric *p*-benzoyl-4,4'-diaminobenzoylaniline can be demonstrated by combining FT-IR and Raman spectroscopies.

3.4. Ultraviolet (UV)-Visible Spectrophotometric Analysis

The spectral absorption peaks in the near ultraviolet and visible regions can reflect the characteristics of conjugated π electrons. The degree of electron delocalization varies in different polymers resulting in differences in their ultraviolet absorption wavelengths. Generally, as the degree of conjugation increases, the absorption peak moves towards longer wavelengths [12]. As shown in **Figure 5**, the absorption of oligomers in the ultraviolet region is related to the degree of conjugation. The peak near 310 nm is the absorption peak of the benzene ring.

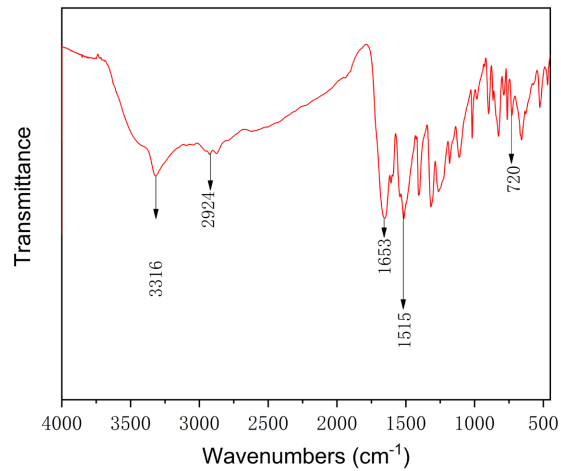


Figure 3. FT-IR spectrum of polymeric *p*-benzoyl-4,4'-diaminobenzoylaniline.

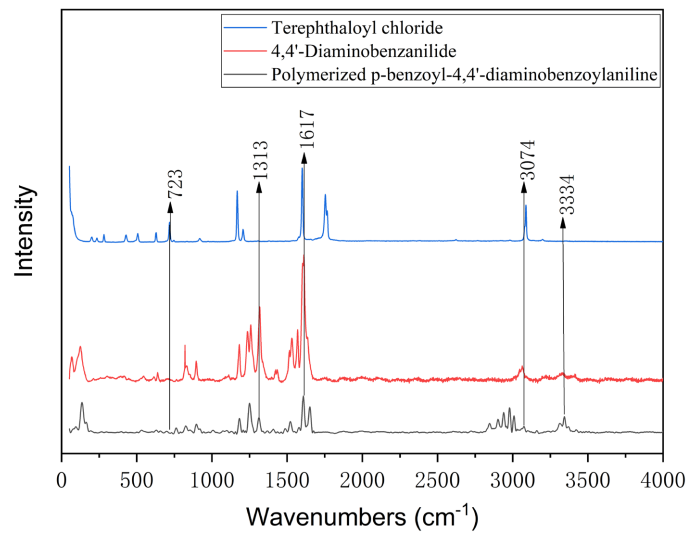


Figure 4. Raman spectrum of polymeric *p*-benzoyl-4,4'-diaminobenzoylaniline.

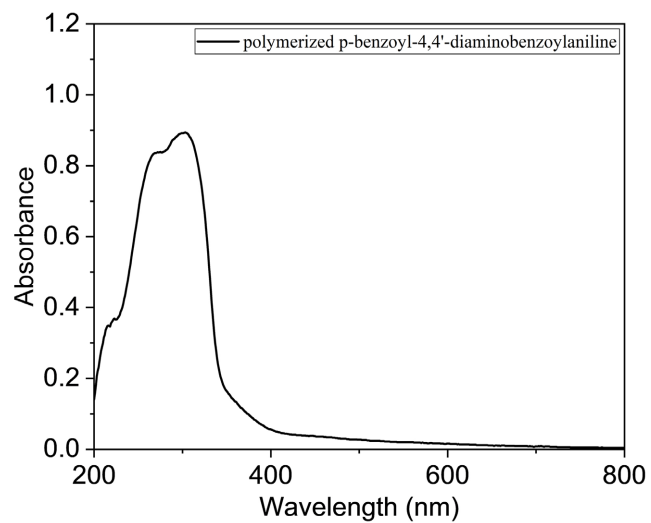


Figure 5. Solid-state UV-visible spectra of polymeric *p*-benzoyl-4,4'-diaminobenzoylaniline.

3.5. Fluorescence Spectroscopy Analysis

The production of fluorescence is completed through two stages: molecular excitation and deactivation. In the molecular excitation stage, the molecule absorbs external energy and enters an excited state, producing excited-state molecules. In the deactivation stage, excited-state molecules return to the ground state *via* non-radiative or fluorescent transitions, releasing fluorescence. A conjugated structure is a favorable structure for increasing fluorescence intensity. The probability of fluorescence generation is increased by enhancing the energy and vibrational intensity of intramolecular π - π jumps. Therefore, blue fluorescence of polymers with conjugated structures can be produced through π - π transitions. When solid-state polymers were excited at 360 nm, the resulting emission spectrum shown in **Figure 6**, which showed a strong blue fluorescence near 420 nm, it was indicated that this polymer has potential applications as a blue electroluminescent polymer material in fields such as light-emitting diodes and fluorescent probes.

3.6. Thermogravimetric Analysis

The sample was heated from room temperature to 800°C under a nitrogen atmosphere with a gas flow rate of 25 mL/min and a heating rate of 10°C/min. The thermal behavior of the polymer was studied by thermal gravimetric analysis (TGA), as shown in **Figure 7**, which is the TGA curve of polymeric *p*-benzoyl-4,4'-diaminobenzoylaniline. During TGA testing, the polymer was measured at a heating rate of 10°C/min under a nitrogen atmosphere of 25 mL/min. It can be seen from the figure that the polymer is stable before 300°C, and significant weight loss begins after 300°C, so it is concluded that it has good thermal stability. There are two main reasons for good thermal stability. First, the amide bond on the molecular chain is *para*-combined with the benzene ring. Due to the conjugation effect, the molecular chain structure is more regular and stable, the

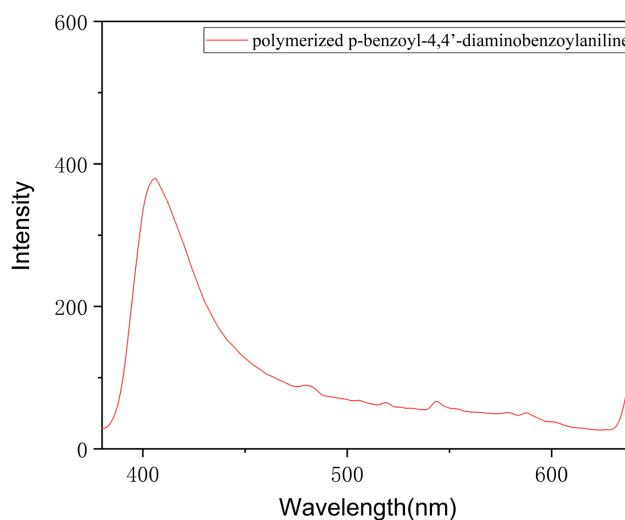


Figure 6. Solid-state fluorescence spectrum of polymeric *p*-benzoyl-4,4'-diaminobenzoylaniline.

molecular rigidity is strong, and the heat resistance is increased. Second, a large number of benzene rings are introduced into the main chain, and the increase of molecular weight makes its decomposition temperature higher, thus improving its thermal stability.

3.7. Electron Microscopy Analysis

The surface morphology of polymeric *p*-benzoyl-4,4'-diaminobenzoylaniline was observed by scanning electron microscopy as shown in **Figure 8**. **Figure 8(a)**,

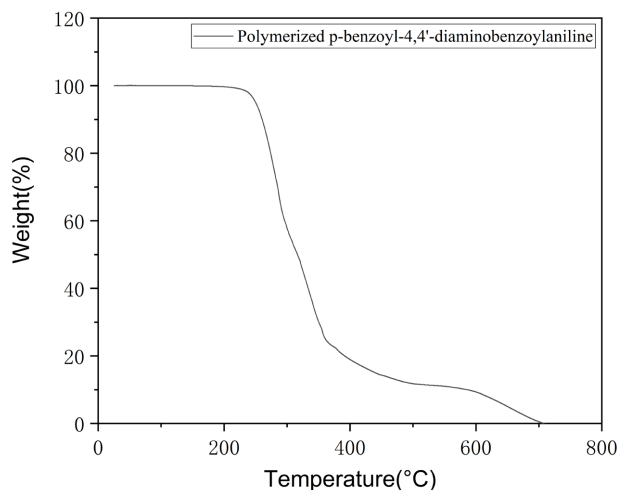


Figure 7. Thermogravimetric analysis (TGA) of polymeric *p*-benzoyl-4,4'-diaminobenzoylaniline.

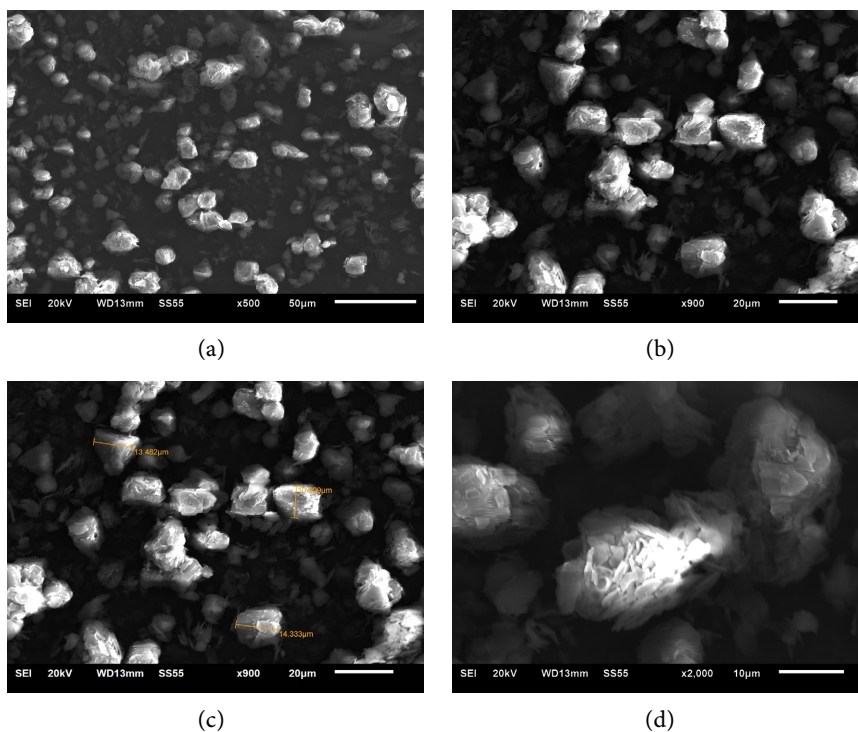


Figure 8. SEM of polymeric *p*-benzoyl-4,4'-diaminobenzoylaniline.

measured at 500 \times , is an image of the overall distribution, where a large number of irregular flakes can be seen. **Figure 8(b)** and **Figure 8(c)** are the images measured at 900 \times , and you can see that the lamellae have agglomerations and are more tightly structured. **Figure 8(d)** is an image measured at 2000 \times , which shows the details of the material, *i.e.*, the particles of the product have an average particle size of approximately 12 μm and exhibit a lamellar structure. The reason for this aggregation behavior of the products may be due to the fact that one of the end groups of *p*-benzoyl-4,4'-diaminobenzoyl-aniline is an amino group, and the amino groups are very prone to form hydrogen bonds with each other.

4. Conclusion

In this study, polymeric *p*-benzoyl-4,4'-diaminobenzoylaniline was synthesized by reacting 4,4'-diaminobenzanilide (4,4'-DABA) with terephthaloyl chloride. The optical properties of the polymer were investigated by FT-IR, UV-vis, Raman, and fluorescence spectroscopies. It was proved that the polymer is stable up to 300 $^{\circ}\text{C}$ and has a relatively high stability by the TGA. Most polyamides do not have luminescence. In this paper, 4,4'-DABA structure was introduced into the main chain of polyamide molecules to change its molecular structure and electron density. Through fluorescence test, it was found that strong blue fluorescence was emitted at 420 nm. As an important part of the development of organic light-emitting diodes (OLEDs), blue fluorescent materials have advantages incomparable to phosphorescent materials, and have become a research hotspot in recent years [13]. OLEDs are mainly used in the field of display, and good thermal stability is also the key to excellent performance of display devices. Therefore, synthetic *p*-benzoyl-4,4'-diaminobenzoylaniline in this paper with high thermal stability and blue fluorescence could be well applied in the field of OLEDs.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Winnacker, M. (2023) Polyamides Derived from Terpenes Advances in Their Synthesis: Characterization and Application. *European Journal of Lipid Science and Technology*, **125**, 202300014. <https://doi.org/10.1002/ejlt.202300014>
- [2] Wang, J.Q., Wang, X.H. and Tao, Y.H. (2023) Sustainable Polyamides Enabled by Controlled Ring-opening Polymerization of 4-Hydroxyproline-Derived Lactams. *Chinese Journal of Polymer Science*, **41**, 728-734. <https://doi.org/10.1007/s10118-022-2871-5>
- [3] Chabaud, G. (2019) Hygromechanical Properties of 3D Printed Continuous Carbon and Glass Fibre Reinforced Polyamide Composite for Outdoor Structural Applications. *Additive Manufacturing*, **26**, 94-105. <https://doi.org/10.1016/j.addma.2019.01.005>
- [4] Sun, Z.H. (2018) Polyamide Modified Technique and the Modified Product Re-

- search Progress. *Textile Science and Engineering*, **35**, 5.
- [5] Zhang, C. (2018) Progress in Semicrystalline Heat-Resistant Polyamides. *e-Polymers*, **18**, 373-408. <https://doi.org/10.1515/epoly-2018-0094>
- [6] Xu, X.W., Yan, C. and Tian, Y.Y. (2023) Aromatic Polyamide Fiber in the Field of Aviation Research Progress. *Aerospace Materials Technology*, **53**, 21-28.
- [7] Su, K., Sun, N., Tian, X., Guo, S., Yan, Z., Wang, D. and Chen, C. (2019) High-Performance Blue Fluorescent/Electroactive Polyamide Bearing *p*-Phenylenediamine and Asymmetrical SBF/TPA-Based Units for Electrochromic and Electrofluorochromic Multifunctional Applications. *Journal of Materials Chemistry C*, **7**, 4644-4652. <https://doi.org/10.1039/C9TC00326F>
- [8] Chiriac, C. and Stille, J.K. (1977) Aromatic Polyamides by a Direct Polycondensation Reaction. *Macromolecules*, **10**, 710-711. <https://doi.org/10.1021/ma60057a044>
- [9] Fan, S.C., Wu, H.M., Jiang, Y.C. and Wang, Y.Y. (2022) Low-Temperature Solution Polycondensation Method for the Synthesis of Poly-*m*-Phenylenediamine Terephthalamide and Characterization. *Synthetic Fiber Industry*, **45**, 6-10.
- [10] Cao, Y.T., Dai, X.F., Hu, Z.M. and Liu, Z.F. (2008) Rheological Property of PPTA Copolymer Solution. *Journal of Donghua University (Natural Science Edition)*, **177**, 545-548.
- [11] Zhang, C., Cao, M., Jiang, S., Huang, X., Mai, K. and Yan, K. (2019) Quick Analysis of Composition of Semi-Aromatic Copolyamide via ¹³C NMR Study. *International Journal of Polymer Analysis and Characterization*, **24**, 4053. <https://doi.org/10.1080/1023666X.2018.1514708>
- [12] Han, Q.R., Lei, Z.Q., Yang, Z.W. and Xia, H.P. (2002) Synthesis of Peripheral Dendrite Polyamide Modified by Small Molecules and Its Fluorescence Properties. *Functional Polymolecular Journal*, **15**, 418-424.
- [13] Liu, W.Q., Cui, Q.Z., and Wu, R.X. (2019) Recent Progress on Blue Delayed Fluorescent Materials and Devices. *Chinese Journal of Applied Chemistry*, **36**, 1-9.