Synthesis and Characterization of Novel Photoactive Polyamide Derived from Substituted Fluorene by Copper (I) Catalyst

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ABSTRACT: A novel polyamide has been successfully prepared through the reaction of 2,7-dibromo-9,9-dioctyl-fluorene with 2,5-dipiperazinedione in the presence of CuI, *N*,*N*′-dimethylethylene diamine (DMEDA) and K_2CO_3 as base mixture and as catalyst. The structures of the monomer and the resulting model compound, as well as the structure, solution viscosity, solubility, molecular weights, thermal behavior, thermal stability, and light absorption and emission spectra of the resulting polyamide were characterized by means of FTIR, elemental analysis, ^{1}H-NMR, ^{13}C-NMR, DSC, TGA, GPC and UV–visible absorption, and fluorescence emission spectrophotometers. The polyamide possesses excellent solubility in organic solvents such as tetrahydrofuran (THF), *N*-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF), ethylacetate, acetone, ethanol, pyridine, chloroform, and toluene at room temperature. The polyamide had inherent viscosity of 0.65 dL/g, and molecular weights of $M_n = 4.25 \times 10^4$ and $M_w = 5.99 \times 10^4$ g/mol. The polyamide had glass transition temperature (T_g) of 138°C, and 10% weight loss at 350°C in nitrogen. The polyamide showed strong UV absorption and blue emission in solution and in solid state.
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Key words: synthesis; fluorene; polyamides; fluorescence; 2,5-diperazinedione

INTRODUCTION

It is known that aromatic polyamides are a class of high temperature resistance polymers with good chemical resistance, thermal stability, low flammability, and very good mechanical properties.[1–4] However, because of their limited solubility in organic solvents, high melting and glass transition temperatures they have difficulties in processing. The introduction of flexible bond into the rigid polymer backbone and reducing crystallinity by using bulky groups along the main chain improve the solubility behavior.[5–7] However, some efforts in using monomers with bulky flexible side groups have been led to polymers with poor solubility in organic solvent.[8]

The search for new electroactive and photoactive polymers has led to a wide use of 9, 9-dialkyl fluorene moieties as building blocks in polymers and small molecules for photonic applications.[9–15] Among different materials, poly(2,7-(9,9-dialkylfluorene))s show particularly interesting optical and electrical properties for the development of blue light-emitting diodes. Intractability and insolubility are a common problem with stiff conjugated polymers with increasing conjugation efficiencies. For the polymers derived from fluorenyl units, substitution on the 9-fluorenyl position enhances the solubility and processability of the resulting polymers.[16] Recent interest in the π-conjugated fluorene polymer materials, with fluoren-2,7-diyl units has led to new methods of synthesis by palladium or nickel catalyzed reaction between the fluorene derivatives.[12,17-19] Transition metal catalyzed C(aryl)—N bond-forming processes plays an important role in organic synthesis in cross-coupling of amides with aryl halides and provides a straightforward route to *N*-arylamides. In recent years, there have been many reports of having focused on deliberate use of ligands to facilitate the copper-catalyzed aryl amidation reaction.[20,21] Following our previous article,[22] we report, in this article, the application of the aforementioned amidation method for the copper-catalyzed coupling of 9,9-dioctyl-2,7-dibromofluorene (DODBF) with δ-valerolactam and 2,5-diperazinedione using K_2CO_3 as a base, CuI and *N*,*N*′-DMEDA as the catalyst to prepare a model compound, and a novel polyamide. The model compound and the polyamide have been fully characterized by using FTIR, ^{1}H-NMR, and ^{13}C-NMR, and elemental analysis. The polyamide has been tested for different physical properties including measurements of molecular weight, viscosity, solubility, thermal stability, UV–visible absorption, and fluorescence emission spectra.

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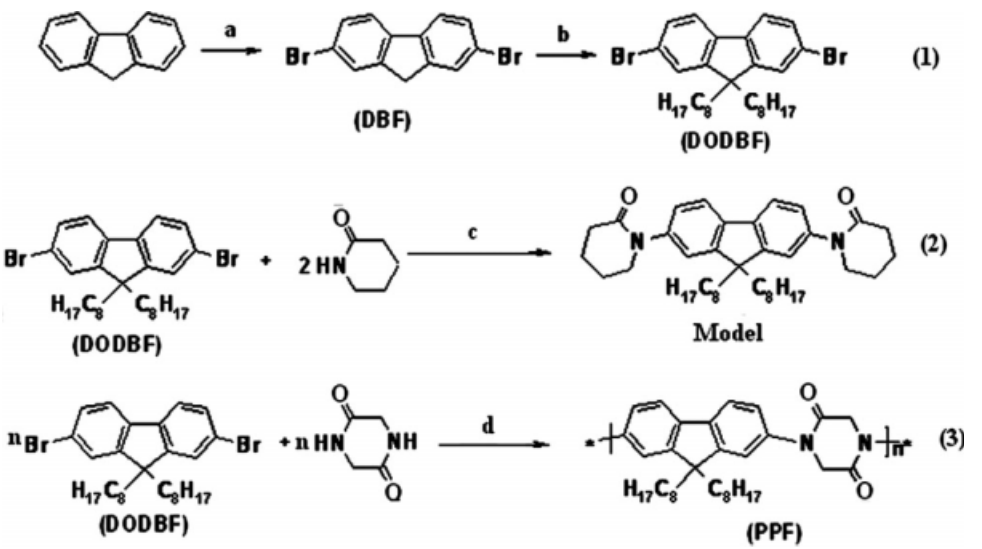

Scheme 1 a) Br_2; CH_3Cl; rt. = 2h. (b) 1-bromohexane; triethylbenzylammonium chloride; DMSO; NaOH 50%; rt. = 5h. (c) CuI; DMEDA; K_2CO_3; toluene; under argon; at 110–115°C; rt. = 7–9h. (d) CuI; DMEDA; K_2CO_3; toluene; under argon; at 110–115°C; rt. = 24h.

EXPERIMENTAL

Materials

Fluorene, bromine, 1-bromooctane, and triethylbenzylammonium chloride were purchased from Merck. *N*,*N*′-dimethylethylenediamine (DMEDA), δ-valerolactam, 2,5-piperazindion, CuI, K_2CO_3, and DMSO were purchased from Fluka. *N*,*N*-dimethylformamide (DMF) from Merck was purified by distillation over calcium hydride under reduced pressure. Toluene from Merck was purified by distillation over sodium. All other materials were used without further purification.

Measurements

FTIR spectra were recorded on a Bruker Vector 22. ^{1}H-NMR and ^{13}C-NMR spectra were measured on a Bruker DRX 500 MHz Advance instrument ($CDCl_3$ and DMSO-d_6 as solvent). Elemental analyses were determined by a Leco CHN-600 analyzer. The UV–visible absorption and fluorescence emission spectra were recorded on a Cecil 5503 and a Perkin–Elmer LS-3B spectrophotometers, respectively. The Inherent viscosity of 0.5 g/dL solution in DMF was measured in an Ubbelohde viscometer at 25°C. Testing of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a DuPont TGA 951 analyzer and a Perkin–Elmer Pyris 6 DSC, respectively, at a heating rate of 10°C/min under nitrogen atmosphere (20 cm^3/min). Weight-average (M_w) and number-average (M_n) molecular weights were determined by gel permeation chromatography (GPC). The GPC measurements were conducted at 30°C with Agilent 1100 GPC instrument equipped with a differential refractometer detector. Four Water (Utrastyragel) columns (300 × 7.7 mm, guard, 10^5, 10^4, 10^3, and 500 Å in a series) were used with THF as eluent at a flow rate of 1 mL/min. The molecular weights were calibrated against polystyrene standards.

Synthesis of the monomer

2,7-dibromofluorene[23]

A 250 mL, two-necked flask equipped with a magnetic stirrer bar and a dropping funnel was charged with fluorene (15 g, 15.04 mmol) and $CHCl_3$ (80 mL). The solution was stirred and bromine (18 mL, 350 mmol) in $CHCl_3$ (20 mL) was added drop wise through the dropping funnel. This is an exothermic reaction, and any rapid addition of the bromine should be avoided. The solution was stirred at room temperature for 20 h in the dark. The solid material was filtered and washed with $CHCl_3$ (100 mL). The product was recrystallyzed in a mixture of ethyl acetate/hexane (5/95 v/v). The yield of the reaction was 97.5% (47.5 g) and the melting temperature of the product was in the range of 159–161°C.

9,9-dioctyl-2,7-dibromofluorene[24]

A 250 mL, two-necked flask equipped with a magnetic stirrer bar was charged with 2,7-dibromofluorene (DBF; 10 g, 30.86 mmol), catalytic amounts of triethylbenzyl ammonium chloride in 50 mL of DMSO, 13 mL of 50% aqueous NaOH, and 1-bromooctane (14.9 g, 77.2 mmol). The reaction mixture was cooled to room temperature and stirred for 5 h.

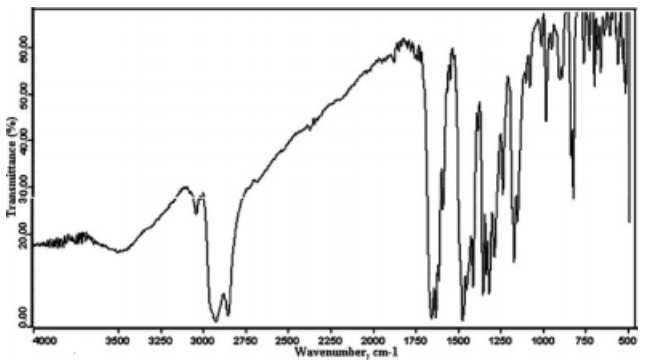

Figure 1 FTIR spectrum of the model.

An excess of ethylacetate was added to the reaction mixture. NaOH precipitate formed was filtered off. The organic layer was washed with dilute HCl (200 mL) and H_2O (250 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure, followed by removal of excess 1-bromooctane by distillation under vacuum. The product was purified three times by recrystallization from hexane, to yield a white crystalline product. The overall yield of this reaction was 96.3% (16.30 g) and the melting temperature of the product was in the range of 51–54°C. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm) showed signals of different protons at δ values of 7.51 (dd, 2H), 7.44 (dd, 2H), 7.43 (s, 2H), 1.90 (m, 4H), 0.98-1.24, (m, 20H), 0.82 (t, 6H), 0.57 (m, 4H).

Synthesis of 2,7-bis(*N*-valerolactame)-9,9-dioctylfluorene model compound

Scheme 1 shows general procedure for the preparation of the model compounds.

A 25 mL, two-necked flask equipped with a magnetic stirrer bar, a condenser, and an argon inlet/outlet tube was charged with DODBF (0.274 g, 0.5 mmol), δ-valerolactam (0.124 g, 1.25 mmol), CuI (0.0192 g, 0.1 mmol, 10 mol %), and K_2CO_3 (0.28 g, 2.03 mmol), briefly evacuated and backfilled with argon. DMEDA (0.021 mL, 2 mmol) and toluene (5 mL) were added and the reaction mixture was stirred at 110–115°C for 7–9 h under argon atmosphere. The resulting bright yellow suspension was allowed to reach room temperature, and then filtered through a 0.5 × 1 cm^2 pad of silica gel eluted with 1 : 1 ethyl acetate-dichloromethane (10 mL). The filtrate was evaporated and then dried in a vacuum oven to afford a brown crystalline product with the yield of 92% and melting range of

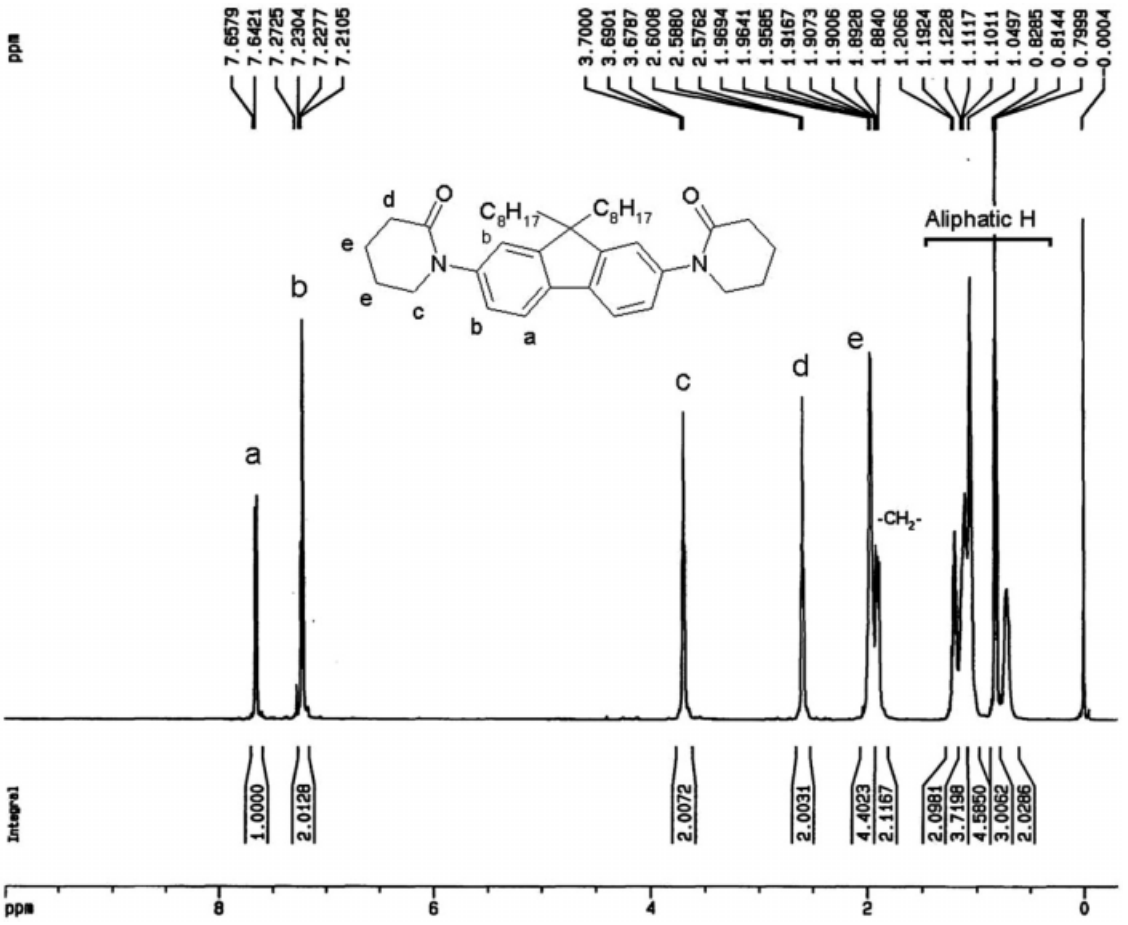

Figure 2 ^{1}H-NMR spectrum of the model.

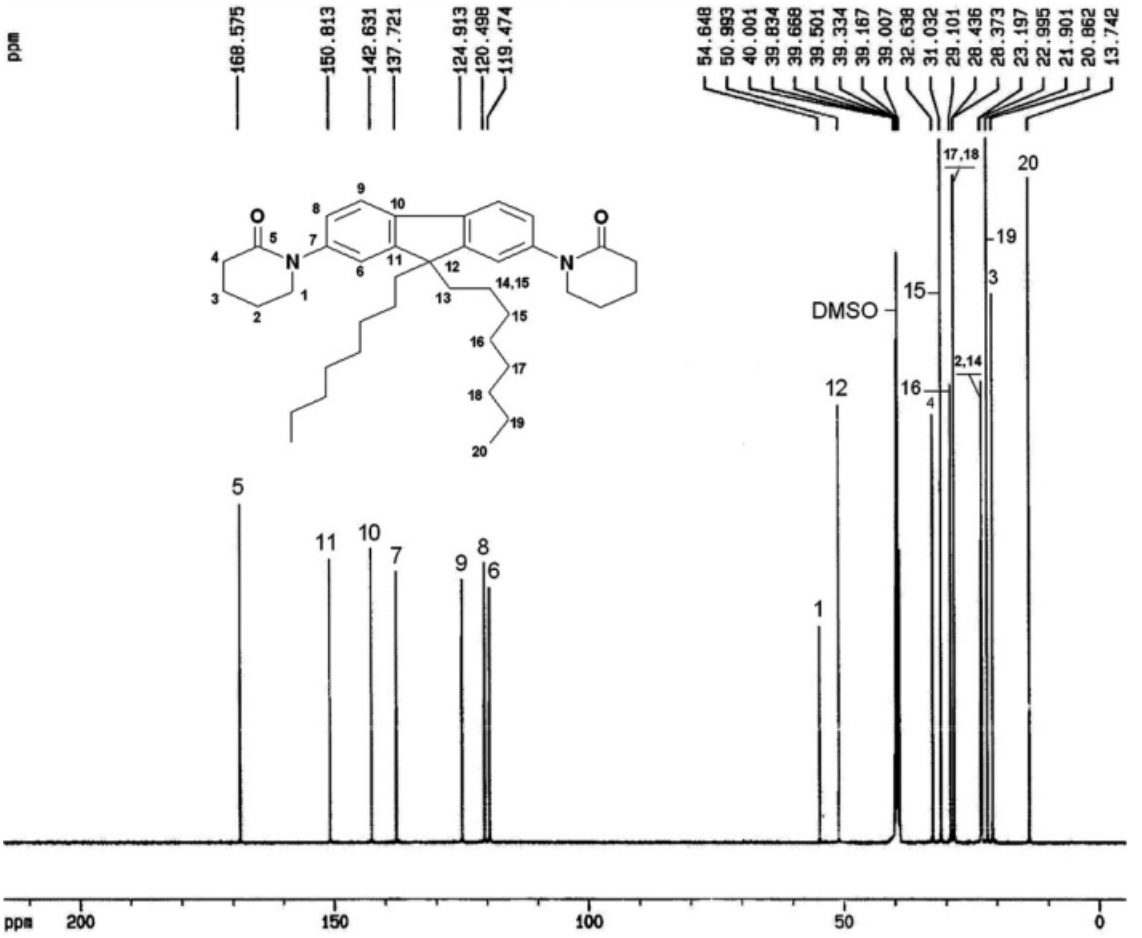

Figure 3 ^{13}C-NMR spectrum of the model.

84.5–87°C. Anal. Calcd for $C_{39}H_{56}N_2O_2$: C, 80.09; H, 9.65; N, 4.79. Found: C, 80.20; H, 9.54; N, 4.68. FTIR of (I) (cm^{-1}): 3047, 2923, 2852 (C—H), 1658 (C=O), 1594, 1464 (C=C), 1405 (C—N), 705 (C=O). ^{1}H-NMR of the model (500 MHz, $CDCl_3$, ppm) showed signals of different protons at δ values of 7.65 (d, aromatic 2H), 7.24 (m, aromatic 4H), 3.69 (t, cycloaliphatic 4H), 2.59 (t, cycloaliphatic 4H), 1.97 (m, cycloaliphatic 8H), 1.29 (t, aliphatic 4H), 1.20 (q, aliphatic 4H), 1.12-1.05 (m, aliphatic 16H), 0.82 (t, aliphatic 6H), 0.72 (b, aliphatic 4H). ^{13}C-NMR of the model (500 MHz, DMSO-d_6, ppm) showed values of 168.57, 150.81, 142.63, 137.72, 124.91, 120.50, 119.47, 54.65, 50.99, 40.001, 32.64, 31.03, 29.10, 28.44, 28.37, 23.20, 22.99, 21.90, 20.86, 31.74.

Synthesis of poly(2,5-(9,9-dioctylflourene) piperazindion) amide (PPF)

A 50 mL, two-necked flask equipped with a magnetic stirrer bar, a condenser, and an argon inlet/outlet tube was charged with CuI (0.076 g, 0.40 mmol, 10 mol%), DODBF (1.096 g, 2 mmol), 2.5-dipiperazinedione (0.285 g, 2.5 mmol), and K_2CO_3 (1.12 g, 8.12 mmol), briefly evacuated and backfilled with argon. DMEDA (0.086 mL, 0.80 mmol) and toluene (15 mL) were added under argon. The reaction mixture was stirred at 110–115°C for 24 h. The resulting mixture was allowed to reach room temperature and then filtered through a 0.5 × 1 cm^2 pad of silica gel eluting with 1 : 1 ethylacetate-dichloromethane (30 mL). The filtrate was evaporated, and then the solid product was dried in a vacuum oven to afford 1.13 g polymer (yield = 85.5%).

Anal. Calcd for $C_{39}H_{56}N_2O_2$ (PPF): C, 79.16; H, 8.86; N, 5.59. Found: C, 79.48; H, 9.02; N, 5.48. FTIR (cm^{-1}): 3035, 2927, 2863 (C—H), 1685 (C=O), 1614, 1475 (C=C), 1405 (C—N), 721(C=O). ^{1}H-NMR (500 MHz, $CDCl_3$, ppm) showed signals of different protons at δ values of δ 7.70 (d, aromatic 2H), 7.35 (m, aromatic 4H), 4.62 (s, cycloaliphatic 4H), 1.96 (b, aliphatic 4H), 1.19–1.07 (m, aliphatic 20H), 0.80 (t, aliphatic 6H), 0.72 (b, aliphatic 4H). ^{13}C-NMR (500 MHz, $CDCl_3$, ppm) showed values of 164.17, 152.30, 139.20, 138.83, 123.67, 120.54, 119.36, 55.73, 53.87, 40.25, 31.76, 29.97, 29.32, 29.21, 23.83, 22.59, 14.07.

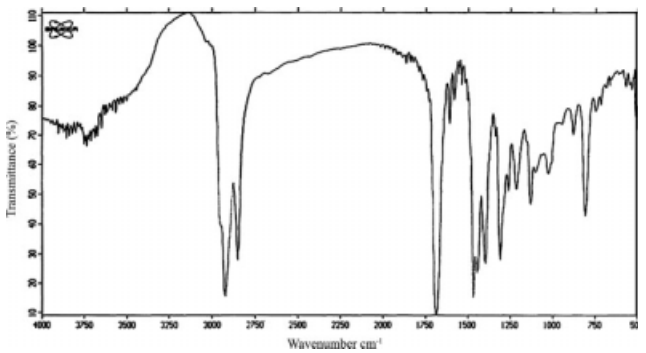

Figure 4 FTIR spectrum of the polyamide.

RESULTS AND DISCUSSION

Synthesis and characterization of the monomer and the model compounds

Scheme 1 shows the synthesis of monomer DODBF, which was prepared according to the procedures given in the literatures.[23,24] FTIR, ^{1}H-NMR, and elemental analysis were used to confirm the structure of this compound. ^{1}H-NMR showed signals in the region of 7.39–7.54 ppm, related to the aromatic protons and in the region of 0.57–1.90 ppm, related to the protons in the aliphatic chains at the 9 position. DODBF was used as a starting material for the preparation of model compound in the reaction with δ-velerolactam and as shown in Scheme 1. The reaction between DODBF and the lactam was conducted in toluene in the presence of CuI, DMEDA ligand, and K_2CO_3 as base at 110–115°C under argon atmosphere. The structure of the model was confirmed by using elemental analyses, FTIR, ^{1}H, and ^{13}C-NMR measurements. Typical spectra are shown in Figures 1–3. The FTIR spectrum of the model shows peaks at ≈ 3040 related to aromatic C—H stretching, at ≈ 1650 related to C=O, at ≈ 1600 and 1470 related to aromatic C=C, and at 1405 related to C—N stretching. In addition to the IR spectra, the elemental analysis values of the model generally agreed well with the calculated values for the proposed structure. The ^{1}H-NMR spectrum of the model shows the characteristic signals at 3.69, 2.59, and 1.97 ppm which are related to the protons of CH_2 groups of the cycloaliphatic ring of valero. The ^{13}C-NMR

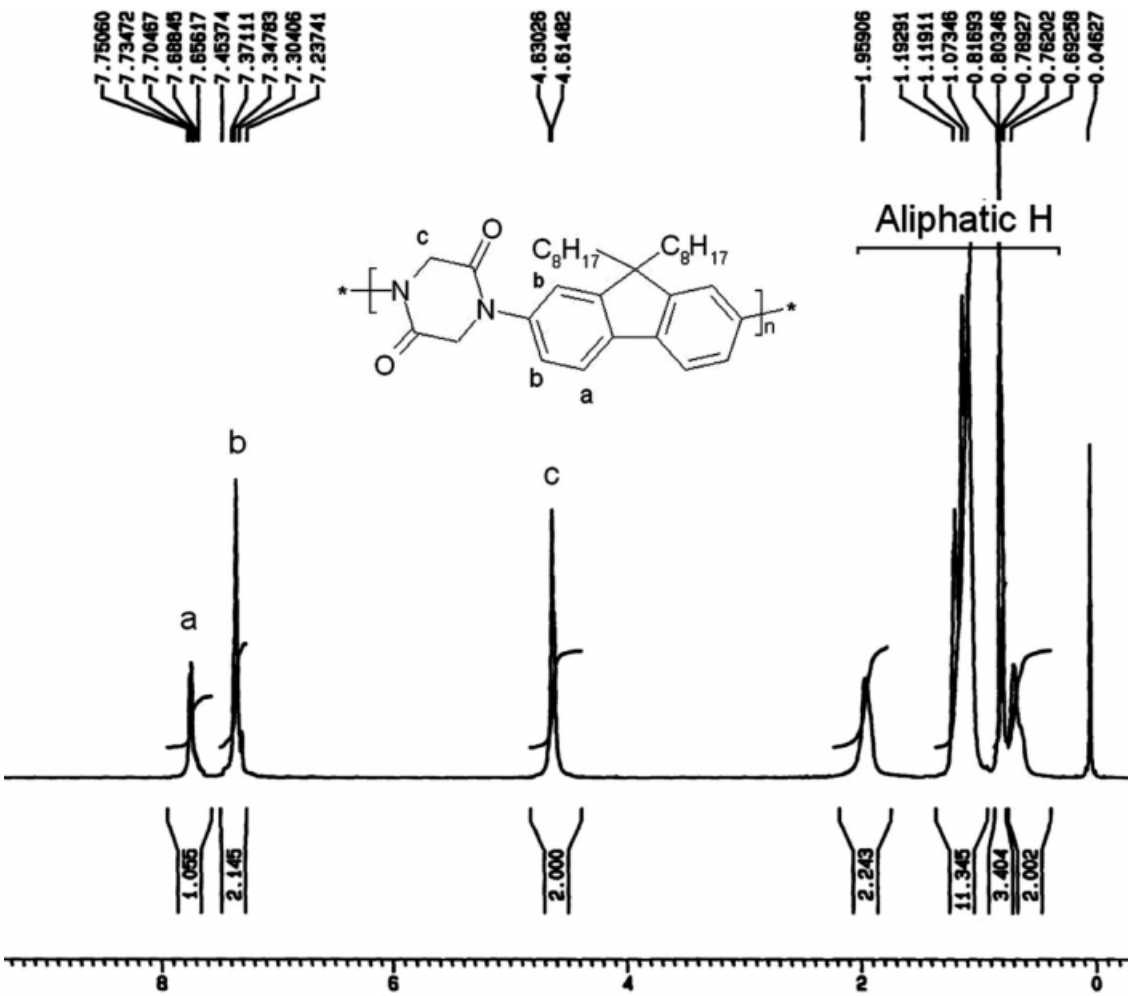

Figure 5 ^{1}H-NMR spectrum of the polyamide.

shows the characteristic signal at 168.57 ppm which is related to the carbon of carbonyl group.

Synthesis and characterization of the polyamide (PPF)

Poly(2,5-(9,9-dioctylflourene) piperazindion) amide (PPF) was prepared in good yield (85.5%) by the reaction between DODBF and 2.5-dipiperazinedione in the presence of inexpensive and air-stable CuI and DMEDA ligand as the pre-catalyst, K_2CO_3 as base in toluene at 110–115°C. The structure of the polyamide was confirmed by the results of elemental analysis and data of spectroscopic methods. FTIR, ^{1}H-NMR, and ^{13}C-NMR spectra of the polyamide are given in Figures 4–6. The FTIR spectrum of the polyamide shows characteristic bands at 3035 cm^{-1} (aromatic, C—H stretching), 2927 and 2863 cm^{-1} (aliphatic C—H stretching), 1685 cm^{-1} (C=O stretching), 1614, 1600, and 1475 cm^{-1} (aromatic C=C), and 1405 cm^{-1} (C—N stretching). The elemental analysis results of the polyamide are in good agreement with the calculated values for the proposed chemical structure. ^{1}H-NMR spectrum of the polyamide shows characteristic signal at 4.62 ppm related to methylene unit in the piperazinedione ring. ^{13}C-NMR spectrum also shows signal at 164.17 ppm which is related to the carbonyl group.

Solubility, viscosity, and molecular weights of the polyamide(PPF)

The polyamide showed excellent solubility in various organic solvents such as NMP, DMSO, DMAC, DMF, THF, chloroform, ethylacetate, acetone, methanol, ethanol, pyridine, benzene, and toluene at room temperature. Comparison of the solubility of the previously reported polyamides[12,16–19,22] with this polyamide indicates that the presence of dioctyl groups at 9-position and particularly, the presence of dipiperazinedione as cycloaliphatic with methylen groups display an enhanced solubility in organic solvents. The inherent viscosity of the polyamide, as a suitable criterion for evaluation of molecular weight, was measured for different polymerization times. The inherent viscosity increased with time of polymerization, from 0.305 g/dL after 5 h to 0.65 dL/g after 24 h and changed to 0.69 dL/g when the reaction time increased up to 30 h. The polyamide exhibits M_n and M_w of 4.25×10^4 and 5.99×10^4 g/mol, respectively.

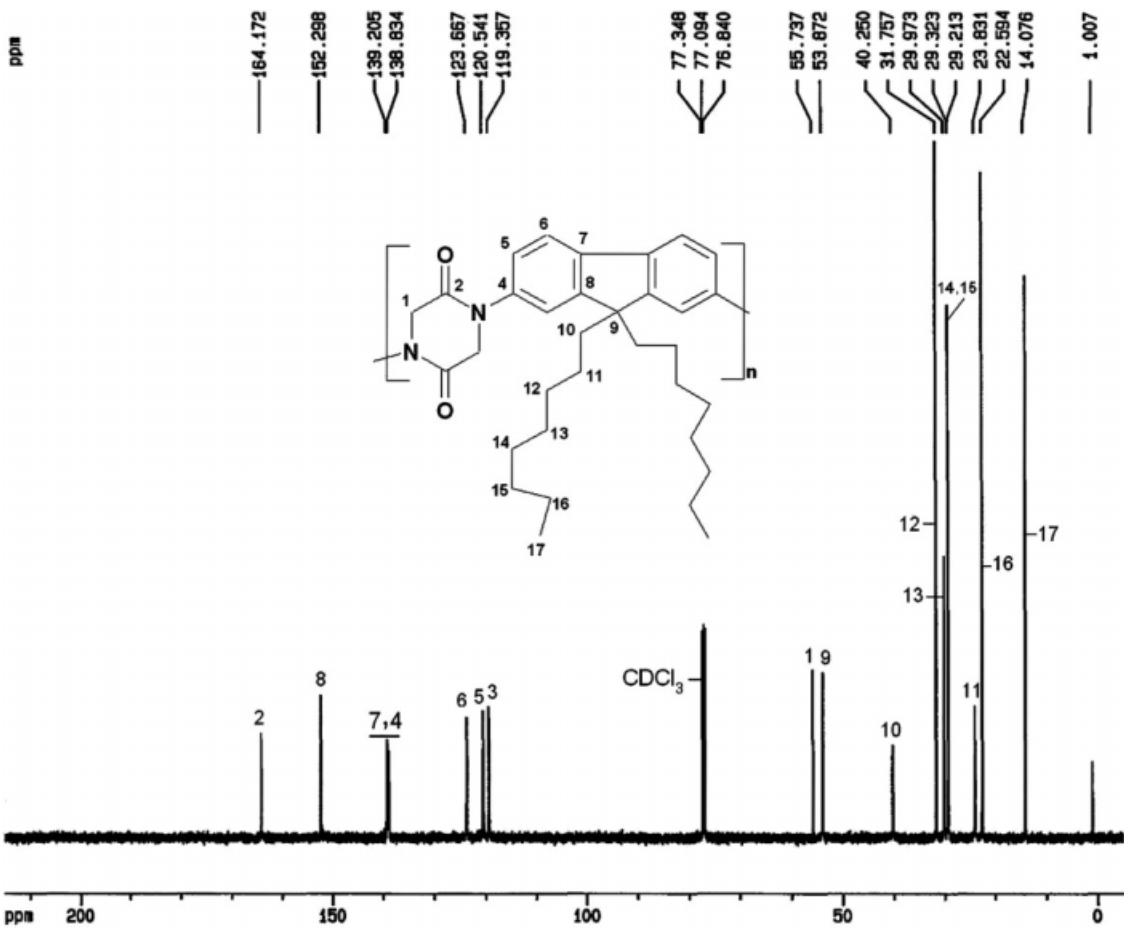

Figure 6 ^{13}C-NMR spectrum of the polyamide.

Thermal properties of the polyamide

The thermal properties of the polyamide were evaluated by TGA and DSC. TGA thermogram of the polyamide in Figure 7 indicates that this polymer possess thermal stability with no significant weight loss up to 350°C. The temperatures for different weight losses of this polyamide in nitrogen atmosphere were determined from the original TGA thermogram showed 10% loss at 350°C, 50% loss at 447°C, and the char yield at 600°C was 25%. DSC thermogram displayed a glass transition temperature (T_g) of 137°C, which is higher than those reported for other polyamides based on the fluorene, such as PDOF of 75°C[25] and PBPF of 91°C.[26] The polymer revealed no clear melting endotherms up to the decomposition temperature on the DSC thermogram.

Photo physical properties of the models and the polyamide

The photophysical properties of the model and the polyamide were measured at room temperature by UV–visible and fluorescence spectroscopy in dilute chloroform solution (0.5 g/dL). Absorption and emission spectra of solutions of the model and the polyamide are shown in Figures 8 and 9, respectively. They show identical absorption spectra from 230 nm to 370 nm with the maximum peak around 315 nm, which corresponds to π–π* transition. The model and the polyamide emit blue light in dilute chloroform solution when excited by the UV light at 366 nm. As shown in Figures 8 and 9, the photoluminescence spectra of the model and the polyamide are identically regular and symmetrical. The maximum emissions of the model and the polyamide in solution were observed at 457 and 470 nm, respectively. Transparent and uniform film of the polyamide was prepared on the quartz glass from its solution in chloroform at room temperature. The solid state absorption and fluorescence spectra of the polyamide were taken in the film deposited on a quartz glass are shown in Figure 10, which are identical with those observed for the solution. The film of polyamide emitted intense blue light by the excitation of UV light at 366 nm. The relatively identical absorption and fluorescence spectra of the polyamide in solution, and as a solid film indicate that there is little difference in the conformations of the polymer in the two states. The introduction of nonconjugated segments into the main chain might depress the excimer formation, and that can be the reason for the regular and symmetrical photoluminescence spectra. It has also been reported[12,15–17] that nonconjugated segments tend to limit formation of undesirable long-wavelength solid-state emission

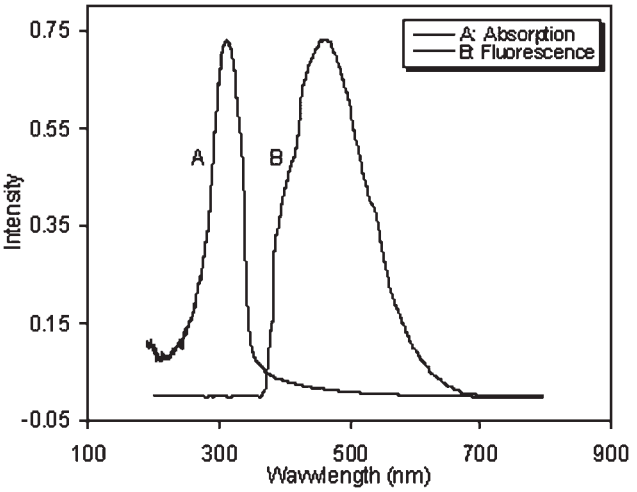

Figure 8 Absorption and emission spectra of the model.

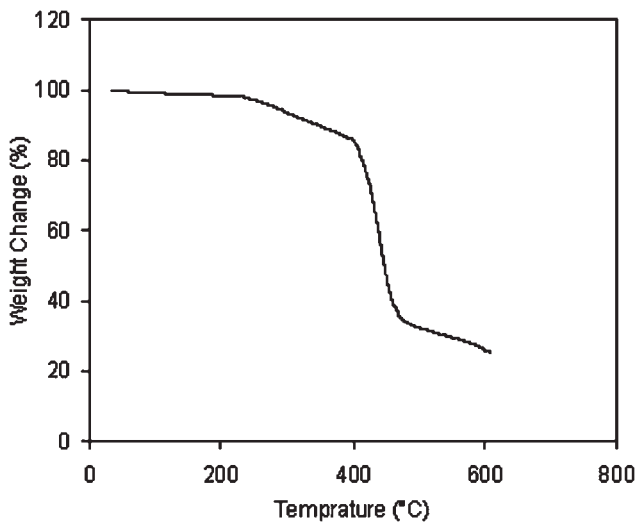

Figure 7 TGA thermogram of the polyamide.

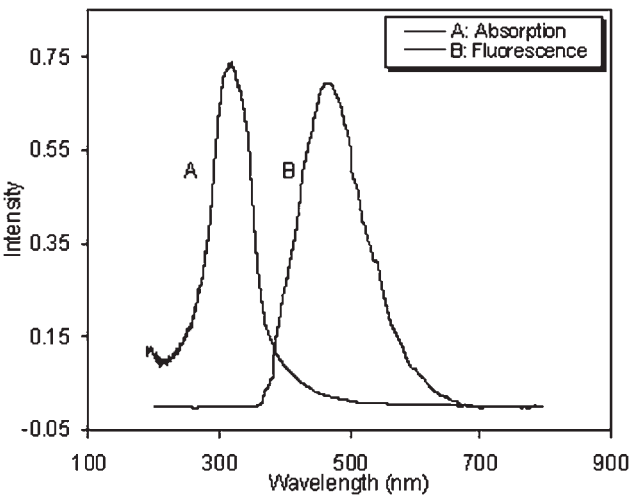

Figure 9 Absorption and emission spectra of the polyamide in solution.

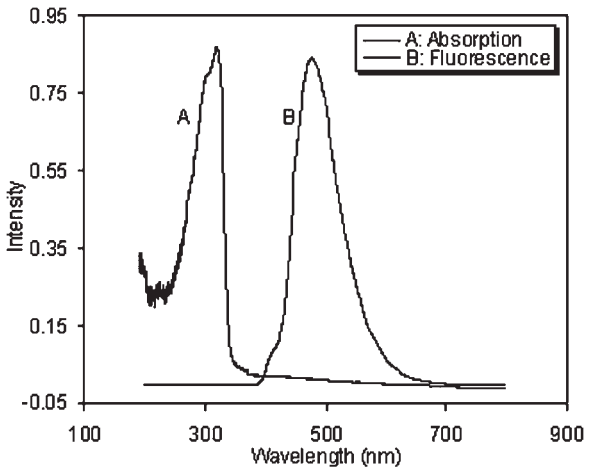

Figure 10 Absorption and emission spectra of the polyamide in solid state.

bands that often formed in some 9,9-dialkyfluorene-based emitters. The prepared polyamide and the model compounds have a low conjugated chain include fluorene core that substituted from 2 and 7 positions with two amides nitrogen. The nitrogen as a donor groups increased the band gap and the π–π* conjugated length which decreased π–π* energy. Therefore, these compounds present promising optical properties.

CONCLUSION

We have successfully used copper-catalyzed aryl amidation method for the synthesis of an aromatic cycloaliphatic polyamide from the reaction between an amide and aromatic dihalide. The synthesized polyamide possesses a T_g of 137°C and acceptable thermal stability with no significant weight loss up to 350°C. The resulting polyamide showed excellent solubility in various common organic solvents such as THF, chloroform, ethylacetate, acetone, methanol, ethanol, benzene, and toluene at room temperature. The polyamide had inherent viscosity of 0.69 dL/g and molecular weights of M_n and M_w were 4.25 $\times$ 10^4 and 5.99 $\times$ 10^4 g/mol, respectively. The nonconjugated model and the polyamide showed good optical properties and emitted blue light, both in solution and in the solid state.

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