Synthesis and Characterization of A New Blue-Light-Emitting Polyimide

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Received September 23, 1997; Revised Manuscript Received May 8, 1998

ABSTRACT: 5,5′-Bis(4-aminophenyl)-2,2′-bifuryl (PFDA) with a well-defined conjugation length was synthesized, and its soluble poly(amic acid) was prepared by polycondensation with pyromellitic dianhydride (PMDA). The PMDA−PFDA polyimide films were obtained from the poly(amic acid) solution through a conventional spin-casting, baking, and thermal imidization process. The PFDA monomer exhibits intense blue photoluminescence with a maximum at 442 nm in a high quantum yield of 0.92, whereas its polyimide film also emits intense blue photoluminescence with double peak maxima at 419 and 436 nm. The polyimide is insoluble in common organic solvents and thermally stable up to 370 °C. Overall, the PMDA−PFDA polyimide can be considered to be a potential candidate material for fabricating optoelectronic devices that emit blue light.

Introduction

Since a diode fabricated with poly(*p*-phenylenevinylene) (PPV) as the emitting layer was first reported to emit green light in 1990,[1] a number of polymeric materials suitable to light-emitting devices (LEDs) have been developed.[2−20] In practice, the most efficient polymeric systems are known to be based on PPV films, which emit basically green light rather than blue light (namely, one of the essential three light elements).[3] There is still a big challenge in developing polymer systems to exhibit highly efficient blue-light emission, which cannot be achieved easily from inorganic materials. There are basically five different approaches in order to develop conjugated polymer systems exhibiting relatively large band gaps that are suitable for blue light emission. The first approach is to synthesize conjugated polymers that are able to emit blue light: poly(*p*-phenylene)[4] and its copolymers with 2,5-dialkoxy-*p*-phenylene blocks[5] and *p*-phenylene ladder segments,[5c,6] poly((2,2,5″,5″-tetraoctyl-*p*-terphenyl-4,4″-ylene)vinylene-*p*-phenylenevinylene),[7] poly((2,3-diphenyl-5-*n*-alkyl-*p*-phenylene)vinylene)s,[8] poly(alkylfluorene)s,[4b,9] and their copolymers containing phenylenebis(divinylene) and dialkyl-*p*-phenylene units,[10] poly(3-methyl-4-cyclohexylthiophene),[11] poly((3-hexylthiophene-ylene)ethynylene)s,[12] and poly(*p*-phenylenebenzobis(imidazole)).[13] The second approach is to make blue-light-emitting blends from green- and yellow-light-emitting polymers with near-blue- or ultraviolet-light-emitting materials: poly(9-vinylcarbazole) blends with PPV and its derivatives and poly(dialkylfluorene) copolymers.[14] The third approach is to make blue-light-emitting bilayer or trilayer films from light-emitting polymers with electron-transporting and hole-transporting materials: bilayer films of poly(*p*-phenylene-2,6-benzobis(oxazole)) with tris(*p*-tolyl)amine-dispersed poly(Bisphenol A carbonate)[15] and of PPV with poly(methyl methacrylate) copolymers bearing 2,5-diaryl-1,3,4-oxadiazoles.[16] The fourth approach is to add blue-light-emitting oligomers into matrix polymers, such as oligomeric PPV dispersed in polymer matrixes.[17] The final approach is to synthesize polymers composed of conjugated segments as a component of the main chain and/or side chain: alternating copolymers of short substituted *p*-phenylenevinylene and with flexible spacer blocks,[18] polysilanes consisting of *p*-penylenevinylene−biphenyl and *p*-penylenevinylene−carbazole derivative blocks,[19] copolymers containing dialkylfluorenes and *N*-alkylcarbazoles,[14c] poly(stilbenyl-*p*-methoxystyrene),[20] polynorbornenes containing short *p*-phenylenevinylene blocks as side groups,[21] and poly(methyl methacrylate)s with distyrylbenzene and oxadiazole side groups.[16a] The last two approaches can provide polymers with a well-defined conjugation length. This is highly desired since the larger distribution in the conjugation length leads to the larger broadness in the emission band.[13c,16a,17−21]

In this study, 5,5′-bis(4-aminophenyl)-2,2′-bifuryl, a new blue-light-emitting diamine monomer with a well-defined conjugation length, was synthesized in accordance to the synthetic scheme shown in Figure 1. A soluble poly(amic acid) precursor was synthesized by polycondensation of the diamine with pyromellitic dianhydride. The soluble poly(amic acid) precursor then was thermally converted to the corresponding polyimide. UV−visible absorption and fluorescence characteristics of the monomer and its polyimide films were investigated. And, the thermal stability of polyimide was examined by thermogravimetry.

Experimental Section

Materials. Pyromellitic dianhydride (PMDA) was purchased from Chriskev Co. and purified by drying at 120 °C for 1 day in vaccum prior to use. *N*-Methyl-2-pyrrolidone (NMP), which was received from Aldrich Co., was purified by distillation over calcium hydride under reduced pressure. All the other chemicals used in this study were obtained from Aldrich Co., and used without further purification.

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S0024-9297(97)01399-5 CCC: $15.00

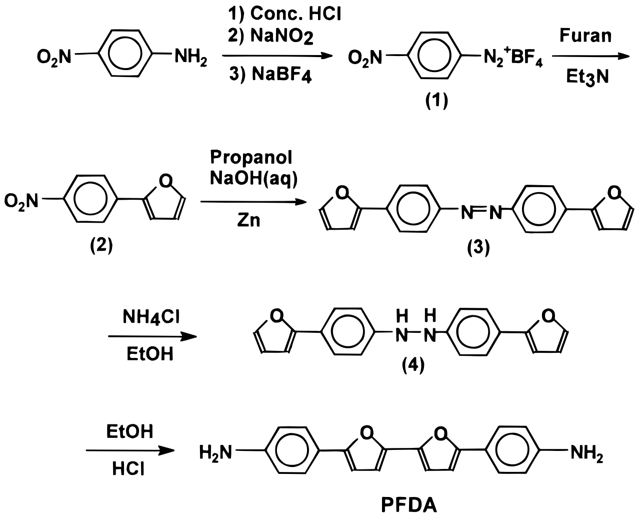

Figure 1. Synthetic scheme of a blue-light-emitting monomer, PFDA.

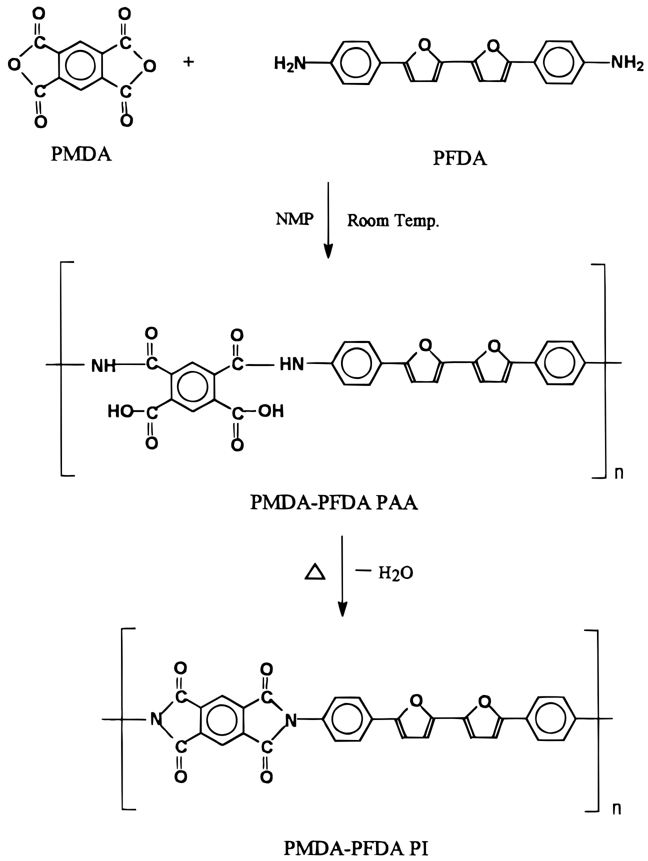

Figure 2. Synthetic scheme of a soluble poly(amic acid) and its polyimide from PFDA and PMDA.

Synthesis of Momomer. *p*-Nitrobenzenediazonium tetrafluoroborate (1). 4-Nitroaniline (10 g, 72.5 mmol) was added to 50 mL of a concentrated HCl/water (1:1 in volume) mixture, followed by stirring for ca. 30 min. Then the reaction mixture was cooled to 0−5 °C using an ice bath, and $NaNO_2$ (6.0 g, 85 mmol) dissolved in 20 mL of water was slowly added. Once the addition was complete, the reaction mixture was stirred for ca. 30 min. $NaBF_4$ (16 g, 140 mmol) was quickly poured into the reaction mixture, followed by stirring further for 1 h before the ice bath was removed. The white powder was filtered off and then washed by several solvents in the following order: cold water, ethanol, and ether. The washed product was dried in a vacuum at room temperature for 1 day. The product (16.8 g) was obtained with a yield of 98.2%. Its melting point (mp) was 161−167 °C.

2-(4-Nitrophenyl)furan (2). **1** (7.5 g, 31.6 mmol) was dissolved with stirring into 40 mL of furan at 0 °C under a dry nitrogen gas flow. Then triethylamine (6.3 mL) in 20 mL of furan was slowly added to the solution through a dropping funnel. Once the addition was complete, 50 mL of hexane was quickly poured into the solution with vigorous stirring. After the product was separated using a chromatographic column filled with silica gel and chloroform eluent, it was recrystallized from an ethanol/water mixture. The purified product was dried at room temperature in a vacuum for 1 day. The product was 4.9 g (82% yield): mp 132−132.9 °C.

Bis(4-(2-furyl)phenyl)diazene (3). **2** (21 g, 111 mmol) dissolved in 150 mL of *n*-propyl alcohol was poured into 17.76 g (444 mmol) of sodium hydroxide in 40 mL of water. Zinc powder (ca. 10 μm in size) (14.5 g, 222 mmol) was added to the mixture with stirring, and the mixture was refluxed for 1 day. A reaction product, sodium zincate, was filtered off while the reaction mixture was hot and then washed with a small amount of *n*-propyl alcohol. The employed *n*-propyl alcohol was distilled from the filtrate. The basic aqueous filtrate was extracted with chloroform, giving the product in orange color. The product was further recrystallized from tetrachloromethane. The final product was dried in a vacuum at room temperature for 1 day. The product of 14.7 g was obtained in a yield of 48.7%: mp 249−251 °C; ^{1}H NMR (δ, $CDCl_3$) 8.3 (dd, 4H, Ph-*H*), 7.75 (d, 4H, Ph-*H*), 7.5 (m, 2H, furyl-*H*), 6.7 (m, 2H, furyl-*H*), 6.5 (m, 2H, furyl-*H*).

Bis(4-(2-furyl)phenyl)diazane (4). Zinc powder (1.2 g) was added to **3** (0.6 g, 1.9 mmol) in 30 mL of acetone under a dry nitrogen gas flow. An aqueous NH_4Cl solution (2 mL) was added to the mixture using a syringe. Then the reaction mixture was vigorously shaken by hand until its red color disappeared. The reaction mixture was poured into 10% aqueous ammonia solution, which was degassed using an aspirator. The white solid was filtered off, followed by washing three times with water. The product was dried in a vacuum at room temperature for 1 day. The product of 0.59 g was obtained in a yield of 98%: mp 156−157 °C; ^{1}H NMR (δ, $CDCl_3$) 7.53 (d, 4H, Ph-*H*), 7.39 (dd, 2H, furyl-*H*), 6.86 (d, 4H, Ph-*H*), 6.4 (m, 4H, furyl-*H*), 5.7 (s, 2H, N*H*).

5,5′-Bis(4-aminophenyl)-2,2′-bifuryl (PFDA). **4** was converted to the diamine form via the benzidine rearrangement reaction described elsewhere.[22] That is, a mixture of 1.0 g (3.16 mmol) of the diazane compound **4** and 50 mL of ethanol was stirred under a dry N_2 atmosphere. The mixture was cooled to 0 °C using an ice bath. A concentrated HCl/ethanol (95%) mixture (1:1 in volume) of 20 mL was added stepwise to the diazane solution of **4** for 1 h. Once the addition was complete, the reaction solution was placed in a refrigerator of ca. 4 °C for 1 day and then filtered. The salt product obtained was converted to the free diamine by treatment with a concentrated aqueous sodium hydroxide solution. The neutralized filterate was extracted with ethyl acetate and the product was separated using a chromatographic column with silica gel and an ethyl acetate/dichloromethane (1:1 in volume) mixture as an eluent solvent. The product separated was further purified by recrystallizing from ethanol, followed by drying in a vacuum at room temperature for 1 day. The product of 0.2 g was obtained in a yield of 20%: *m*/*e* 316 (M^+); mp 203−205 °C; ^{1}H NMR (δ, acetone-d_6) 7.5 (d, 4H, Ph-*H*), 6.72 (d, 4H, Ph-*H*), 6.68 (d, 2H, furyl-*H*), 6.62 (m, 2H, furyl-*H*), 4.88 (s, 4H, NH_2) (see Figure 2). Anal. Calcd for $C_{20}H_{16}N_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.68; H, 5.02; N, 9.04.

Synthesis of Poly(amic acid). Poly(amic acid) was prepared in a glovebox filled with dry nitrogen gas by slowly adding 1.3970 g (7.390 mmol) of the purified PMDA to 2.3358 g (7.390 mmol) of PFDA dissolved in 36 mL of NMP with vigorous stirring (see Figure 3). Once the dianydride addition was complete, the reaction flask was capped tightly and stirring was continued for 1 day to make the polymerization mixture completely homogeneous. The poly(amic acid) solution was filtered with silver metal membranes of 1.0 μm pore size, sealed tightly, and stored in a refrigerator of −4 °C before use.

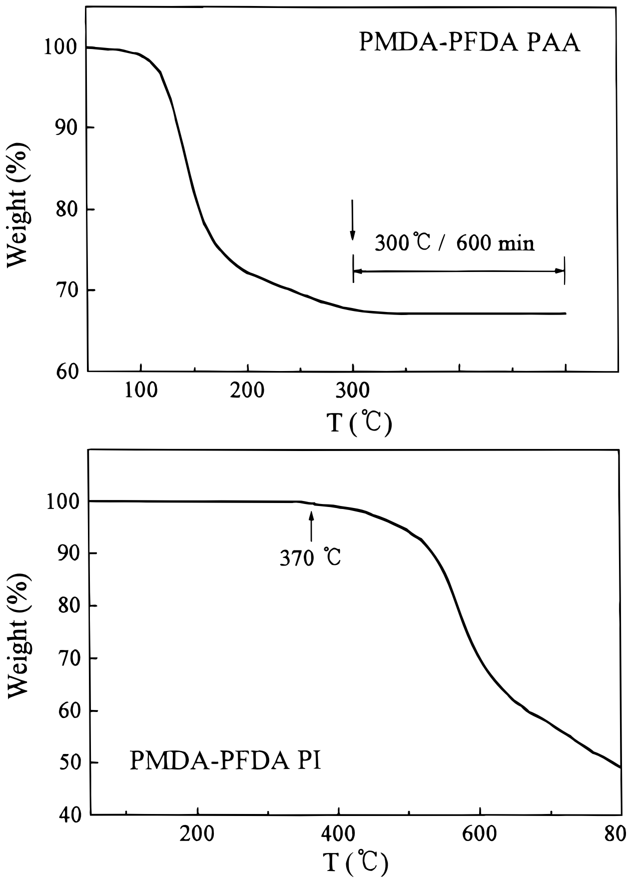

Figure 3. TGA diagrams of PMDA−PFDA poly(amic acid) and its polyimide: (top) poly(amic acid) baked at 80 °C for 1 h; (bottom), polyimide prepared at 300 °C for 1 h. TGA runs were carried out with a ramping rate of 5.0 K/min under a dry nitrogen gas flow.

For the synthesized poly(amic acid), the intrinsic viscosity [η] was measured in NMP at 25.0 °C using an Ubbelohde suspended level capillary viscometer as a method described in the literature.[23] To minimize the polyelectrolyte effect in the viscosity measurement, NMP was purified by distillation over calcium hydride under reduced pressure and further treated with 0.02 M P_2O_5, followed by filtration before use.[23] The relative and specific viscosities were measured at four different concentrations over the range of 0.20−0.80 g/dL, and the [η] value was determined by extrapolations of the reduced and inherent viscosities to infinite dilution. The [η] was determined to be 0.661 dL/g.

Preparation of Polyimide Films. The poly(amic acid) solution of a concentration of 9.1 wt % was spin-coated on glass substrates, followed by baking on a hot plate at 80 °C for 1 h. The baked precursor films were thermally imidized in an oven with a dried nitrogen gas flow by a three-step imidization protocol: 150 °C/30 min, 230 °C/30 min, and 300 °C/60 min. The ramping rate was 2.0 K/min for the first two steps and 5.0 K/min for the final step. After the thermal imidization, the samples were cooled to room temperature with a rate of 10.0 K/min. The thickness of the imidized films was in the range of 15−20 μm. The films were taken off the glass substrates with the aid of deionized water, followed by drying for 2 days at 50 °C in a vacuum of 5 × 10^{-4} Torr. For measurements of physical properties, films were cut into appropriate sizes. In addition, for UV−visible spectroscopic measurements, polyimide films of 0.1−2 μm thickness were prepared on quartz substrates from a diluted solution (1−2 wt % solid content) of the poly(amic acid).

Characterization. The product obtained at each synthetic step was identified by ^{1}H NMR spectroscopy. ^{1}H NMR spectra were measured using a Bruker ASPECT 300 MHz NMR spectrometer in acetone-d_6 or chloroform-d_1 solvent. Chemical shifts were calibrated with the chemical shift of a solvent used. Melting points were determined using a Thomas-Hoover capillary melting point apparatus. In addition, for the newly synthesized diamine monomer, the molecular weight was determined using a mass spectrometer (Hewlett-Packard HP-5970) coupled with a gas chromatographic analyzer (Hewlett-Packard HP-5890). Elemental analysis was carried out using an Elementar Vario analyzer.

Thermogravimetric analysis (TGA) was carried out for the baked poly(amic acid) and its polyimide using a Perkin-Elmer thermogravimeter (Model TGA7) under a dry nitrogen gas flow. That is, a baked precursor sample was heated to 300 °C with a rate of 5.0 K/min, then soaked at 300 °C for 1 h, and finally cooled to 50 °C. Then the imidized sample was again heated to 800 °C with a ramping rate of 5.0 K/min.

For the new diamine monomer and its polyimide, excitation and photoluminescence spectra were measured at room temperature using a fluorescence spectrophotometer (Shimadzu RF-500) with a Xenon lamp. For both excitation and emission monochromators, band-passes were 2 nm, respectively. Photoluminescence behavior of the new monomer was investigated for its solution with a concentration of 1.5 × 10^{-5} g/mL in 1,4-dioxane. The excitation wavelength employed was 340 nm. On the other hand, the polyimide in films was excited with a wavelength of 380 nm in a front-face arrangement in order to minimize the self-absorption. The size of polyimide specimens was 10 × 30 mm. UV−visible spectroscopic measurements were performed using a Hewlett-Packard spectrometer (Model HP-8452A).

In addition, the relative fluorescence quantum yield (Φ_f) of the diamine monomer was measured by comparing the ratio of the fluorescence emission intensity maximum to UV absorbance at the excitation wavelength used for the sample with that of a standard.[7,24] Here, quinine sulfate was employed as a standard: quinine sulfate in 1 N H_2SO_4 at 25 ± 1 °C has been reported to have $\Phi_f = 0.57$ when excited at 348 nm.[10,25] All sample solutions were freshly prepared in dry 1,4-dioxane and then used within 2 h. Absorbances of all solution samples were controlled to be 0.07−0.09 by changing concentrations, to avoid any inner filter effect.

Results and Discussion

The soluble poly(amic acid) (PMDA−PFDA PAA) was prepared in aprotic NMP solvent from the low-temperature polycondensation of PFDA and PMDA (see Figure 2). The poly(amic acid) solution was spin-cast on glass substrates, followed by baking at 80 °C. The thermal imidization of the precursor film was investigated under a dry nitrogen atmosphere by thermogravimetry, as shown in Figure 3 (top). In the heating run, the weight loss over 100−186 °C is due to the removal of residual NMP solvent as well as the byproduct (that is water) of imidization in part. The further weight loss over 186−300 °C is due to the removal of the byproduct as well as the continuous removal of residual solvent. Then, the weight loss levels off during soaking for 1 h at the final imidization temperature, 300 °C.

The sample imidized in the sample stage of the thermogravimeter was cooled to room temperature and then reheated to 800 °C with a rate of 5.0 K/min, to investigate its thermal stability. The result is illustrated in Figure 3 (bottom). The polyimide apparently did not show a weight loss up to ca. 370 °C. However, weight loss starts at ca. 370 °C and then gradually increases until ca. 520 °C. Thereafter, the rate of the weight loss is significantly increased with increasing temperature. Consequently, the thermal stability of this polymer is limited up to ca. 370 °C.

According to the TGA results in the present study as well as the spectroscopic measurements of conventional poly(amic acid) precursors appearing in the literature,[26]

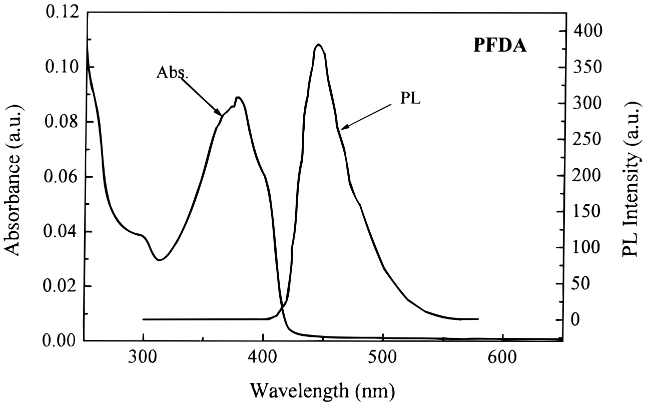

Figure 4. UV−visible absorption and photoluminescence (PL) spectra of PFDA dissolved in 1,4-dioxane with a concentration of 1.5 × 10^{-5} g/mL. The excitation was at 340 nm.

all the polyimide films were prepared by imidizing the baked precursor films at 300 °C for 1 h as described in the Experimental Section. Like conventional aromatic polyimides, the polyimide was not soluble in common organic solvents, including NMP, dimethylacetamide, dimethyl sulfoxide, and toluene. The polyimide films were brittle, so that both stress−strain and dynamic mechanical thermal analysis, which can give mechanical properties and glass transition, respectively, could not be conducted. The glass transition temperature of the polyimide could not be identified using a differential scanning calorimeter.

The UV−visible spectrum of PFDA dissolved in acetone (1.5 × 10^{-5} g/mL) exhibits a broad featureless absorption with the lowest energy absorption maximum at ca. 376 nm (see Figure 4). This absorption is considered to be the $\pi-\pi^*$ transition, leading to the formation of a singlet exciton. With this UV−visible absorbance characteristic, the monomer solution was excited at a wavelength of 340 nm, which provides the best fluorescence spectrum. The emission spectrum appeared to be a single peak over 410−540 nm, showing a peak maximum of 442 nm. The full-width at half-maximum (fwhm) of 43 nm is relatively very narrow. That is, the PFDA emits an intense blue fluorescence.

For PFDA monomer, relative fluorescence quantum yield (Φ_f) was measured to be $\Phi_f = 0.92$ in dioxane solution. This quantum yield is much higher than those of 1,8-diphenyloctatetraene (0.09)[27] in cyclohexane and (3-hexylthiophene-ylene)ethynylene derivatives (0−0.21, depending on the conjugation length)[12] in tetrahydrofuran (THF). Furthermore, Φ_f is comparable to those of some *p*-phenylenevinylene derivatives (0.8 for 1,4-bis(2,5-dioctylstyryl)benzene[7] in THF and 0.94 for 1,4-bis((4-isopropylphenyl)ethenyl)benzene[27] in cyclohexane), which are known as high quantum yield model compounds including the *p*-phenylenevinylene unit.

On the other hand, the polyimide film also exhibited a very broad featureless absorption at less than ca. 470 nm, as shown in Figure 5. When the film was excited at 380 nm (the maximum excitation wavelength), the best emission spectrum was obtained (see Figure 5). The emission spectrum is observed over the range of 390−520 nm. The spectrum exhibited two peak maxima, one at 419 nm and the other at 436 nm, indicating blue light emission. The polyimide consists of two different kinds of chromophores, PMDA and PFDA units. However, the fluorescence of the PMDA unit is relatively weak.[28] Therefore, the photoluminescence of the polyimide might be attributed mainly from the PFDA chromophore unit. The two peaks in the emission spectrum may be a vibronic structure instead of two separate peaks. In addition, for the spectrum, fwhm is 63 nm, which is relatively broader than that of the PFDA monomer. This may result mainly from the nature of vibronic structure in the emission spectrum. However, the fwhm still is relatively very narrow in comparison to those of other light-emitting polymers, such as poly(*p*-phenylenevinylene) and its copolymers.[1,7,18]

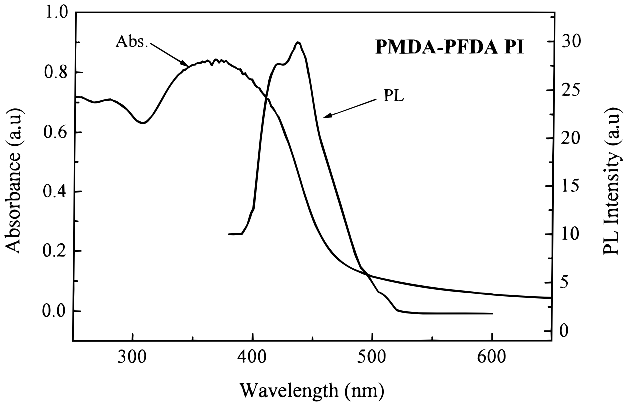

Figure 5. UV−visible absorption and photoluminescence (PL) spectra of the PMDA−PFDA polyimide films, which were imidized at 300 °C for 1 h: the film thickness was 0.6 μm for the measurement of the UV−visible spectrum and 15.5 μm for the measurement of the PL spectrum. The excitation was at 380 nm.

The emission spectrum of the polyimide was slightly blue-shifted, compared to that of the PFDA monomer. This may be due to two reasons in the following. First, the fluorescence of a chromophore is generally influenced by the nature of a solvent used in dissolving it. Thus, the emission peak of the PFDA may be shifted with varying its solvent. Second, the PMDA unit in the polyimide is cooperatively worked out with the PFDA unit to blue-shift the emission spectrum slightly. In general, the amino group is known to have electron donorability, so that the two amino end groups in the PFDA monomer play as electron donors. In contrast, both carbonyl and phenyl groups are known to be electron withdrawing groups. Thus, the PMDA unit in the polyimide plays as an electron withdrawing group to the PFDA unit, positively contributing to the blue-shift in the emission spectrum.

The UV−visible absorption spectrum of the PFDA is not overlapped with its emission spectrum (see Figure 4). However, for the polyimide the absorption spectrum is overlapped partially with the emission spectrum over the range of 390−480 nm, as shown in Figure 5. The absorption in the overlapped wavelength region may affect the emission performance of the polyimide positively or negatively. For this reason, excitation spectra were measured at the maximum emssion wavelengths (419 and 436 nm), respectively. As shown in Figure 6, the excitation spectra resemble each other except for a slight difference in the intensity. These spectra show two peak maxima, one at 380 nm and the other at 397 nm. These excitation spectra are relatively narrower than the absorption spectrum. Over the range of 390−450 nm, the excitation intensity decreases significantly with increasing wavelength. However, the excitation intensity is almost negligible above 450 nm. These indicate that the absorption over only 390−450 nm contributes to the emissions at 419 and 436 nm in a

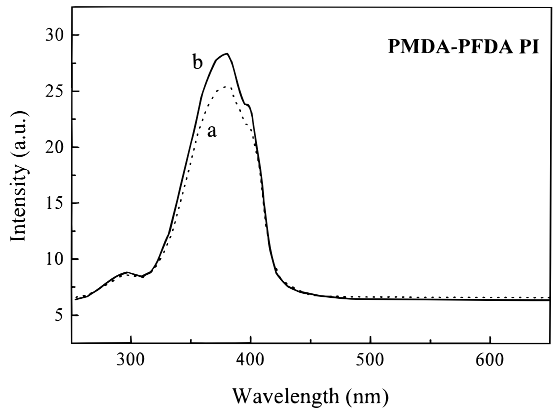

Figure 6. Excitation spectra of the 15.5 μm thick PMDA−PFDA polyimide film, which was imidized at 300 °C for 1 h. Excitation spectra were scanned at the maximum emission wavelengths: (a) 419 nm; (b) 436 nm.

certain level, depending upon the wavelength, and that over 450−480 nm does not contribute to the emissions. Overall, the absorption over the overlapped wavelength region may contribute negatively to the emissions at 419 and 436 nm.

For the polyimide film, relative fluorescence quantum yield could not be measured in this study because of no availability of a chromophore standard with a known quantum yield in films in our laboratory. However, the polyimide consisting of PFDA units with a high fluorescence quantum yield is expected to have a high quantum yield in fluorescence.

Conclusions

We have synthesized and characterized a new type of diamine monomer, PFDA, which has a well-defined conjugation length, and its soluble poly(amic acid) from polycondensation with PMDA. The poly(amic acid) solution was fabricated to polyimide films through a conventional spin-casting, baking, and thermal imidization process. The new PFDA monomer exhibited very intense blue photoluminescence with a maximum at 442 nm, whereas its polyimide also emitted intense blue photoluminescence with double peak maxima at 419 and 436 nm. PFDA exhibits a high fluorescence quantum yield of 0.92 in dioxane solution, so that its polyimide film is expected to have a high fluorescence quantum yield. The polyimide is thermally stable up to 370 °C. Therefore, the PMDA−PFDA polyimide is a potential candidate material for fabricating optoelectronic devices that can emit blue light.

Acknowledgment. This study was supported in part by the Center for Advanced Functional Polymers at KAIST (Contract No. 97K3-0307-01-04-3) (funded by the Korea Science & Engineering Foundation (KOSEF)), KOSEF (Contract No. 95-05-01-08-01-3), and the Basic Science Research Institute Program (Contract No. BSRI-97-3438) of the Ministry of Education, Korea.

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MA971399N