

Synthesis and blue light-emitting characteristic of rod-like poly(4,4'-biphenylene pyromellitimide) with furyl side groups

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Abstract

A new 2,2'-bis(furyl)benzidine (FurylBZ) with a well-defined conjugation length was synthesized, and its polyimide was prepared through thermal imidization of the poly(amide acid) obtained from the polymerization with pyromellitic dianhydride. FurylBZ monomer and its polyimide film were characterized to exhibit intense blue light emission with a relatively narrow peak width in the photoluminescence. The relative fluorescence quantum yield was measured at room temperature to be 0.52 for FurylBZ in 1,4-dioxane and 0.074 for the polyimide in films. The polyimide was thermally stable up to 400°C. The polyimide is amorphous, due to the bulky furyl side groups. However, the polyimide chains were favorably aligned in the film plane due to the rod-like chain characteristic. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Soluble poly(amide acid); Polyimide; Well-defined conjugation length

1. Introduction

In the fabrication of optoelectronic devices, conjugated polymers have many potential advantages, such as good mechanical and electro-optical properties, various choices of chemical structures, and easy processability, in comparison to inorganic semiconductors. Because of the advantages, conjugated polymeric systems have gained great attention from both academia and industry. Light-emitting devices (LEDs) fabricated with a conjugated polymer, poly(*p*-phenylenevinylene) (PPV), were first introduced in 1990 [1]. In particular, this demonstration has stimulated polymer communities throughout the world to become involved in the research and development of light-emitting polymeric materials. Consequently, a number of polymeric materials suitable for LEDs have been reported so far [2–5].

In practice, the most efficient polymeric systems are known to be based on PPV films, which can emit basically green light rather than blue light [4]. The emission of blue light, which is one of the three essential light elements, is known not to be achieved easily from inorganic materials. Therefore, there is still a big challenge in developing

polymeric systems to exhibit highly efficient blue light emission. The development of such polymeric systems has been attempted in several different ways, including homopolymers, copolymers, and blends. In general, the longer conjugation length in a polymer shifts emission spectrum to the longer wavelength region and the higher distribution in the conjugation length causes larger broadness in the emission band. Thus, a well-defined conjugation length is highly desired in designing polymer systems to emit specifically blue light. To date poly(*p*-phenylene) [6,7], poly(3-methyl-4-cyclohexylthiophene) [8], poly(alkylfluorene) [9], PPV copolymers with limited conjugation lengths [10–14], and oligomeric PPV dispersed blends [15] have been reported as blue light-emitting polymeric materials.

In this study, a new benzidine monomer having furyl groups as side group substituents was synthesized: 2,2'-bis(furyl)benzidine (see Fig. 1). Its processable poly(amide acid) was prepared in *N*-methyl-2-pyrrolidone by the polycondensation with pyromellitic dianhydride, and thermally converted to the polyimide. Fluorescence characteristics of the new monomer and its polyimide were investigated. In addition, the polyimide was further examined by thermogravimetry and X-ray diffraction.

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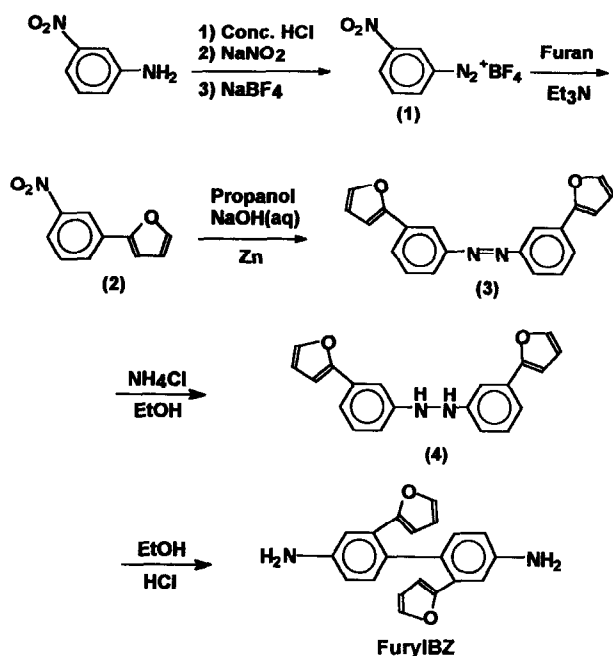


Fig. 1. Synthetic scheme of a new blue light-emitting monomer, 2,2'-bis(furyl)benzidine (FurylBZ).

2. Experimental

2.1. Synthesis of monomers

All the chemicals used in the synthesis of monomer were obtained from Aldrich Chemical Company, and used without further purification. Products obtained at each synthetic step were identified in acetone-*d*₆ and CDCl₃ solvent using a proton nuclear magnetic resonance (¹H n.m.r.) spectrometer (Model ASPECT 300 MHz NMR, Bruker Company). Melting points were determined using a Thomas Hoover capillary melting point apparatus. Elemental analyses were carried out using an Elementar Vario analyzer.

2.1.1. *m*-Nitrobenzenediazoniumtetrafluoroborate (**1**)

A mixture of 10 g (72.5 mmol) of *m*-nitroaniline and 50 ml of conc. HCl/water mixture (1:1 in volume) was stirred for *ca.* 30 min. The mixture was cooled to 0–5°C using an ice bath. NaNO₂ (6.0 g, 85.0 mmol) in 20 ml water was added slowly to the *m*-nitroaniline solution. Once the addition was completed, the reaction mixture was further stirred for *ca.* 30 min. Then, NaBF₄ of 16 g (140 mmol) was poured quickly into the reaction mixture, followed by stirring for 1 h prior to removing out the ice bath. The white powder was filtered, and washed with several solvents in the following sequence: cold water, ethyl alcohol, and ether. The product was dried in vacuum at room temperature for 1 day. The product of 16.8 g was obtained with a yield of 97.8%; m.p. 161–167°C.

2.1.2. (3-Nitrophenyl)furan (**2**)

m-Nitrobenzenediazoniumtetrafluoroborate (**1**) (7.5 g,

31.6 mmol) was dissolved in 30 ml furan under a dried N₂ atmosphere, and cooled down to 0°C. Triethylamine (4.5 g, 44.6 mmol) in 20 ml furan was slowly added to the solution through a dropping funnel. Once the addition was completed, hexane of 50 ml was quickly poured into the reaction mixture with stirring. The product was separated through a chromatographic column with silica gel and hexane/ethyl acetate (3:2 in volume) mixture as eluent solvent, and recrystallized from an ethanol/water mixture, followed by drying in vacuum at room temperature for 1 day. The product of 3.8 g was obtained in a yield of 63.6%; m.p. 42.8–44.5°C.

2.1.3. Bis(3-(2-furyl)phenyl)diazene (**3**)

(3-Nitrophenyl)furan (**2**) (3.4 g, 18 mmol) in 50 ml of *n*-propyl alcohol was poured into 2.9 g (72 mmol) of sodium hydroxide dissolved in 20 ml of water. Zinc powder (2.3 g, 36 mmol) was added to the mixture with stirring and refluxed for 1 day. A reaction product, sodium zincate was filtered while the reaction mixture was hot, and washed with a small amount of *n*-propyl alcohol. All the *n*-propyl alcohol employed was distilled out from the filtrate. The basic aqueous filtrate was extracted with chloroform, giving the product in orange color. The product was further recrystallized from ethanol. The final product was dried in vacuum at room temperature for 1 day. The product of 2.7 g was obtained in a yield of 55.1%; m.p. 124–125.5°C; ¹H n.m.r. (δ, DMSO-*d*₆), 8.52 (t, 2H, furyl-*H*), 7.98–7.64 (m, 8H, Ph-*H*), 7.50 (dd, 2H, furyl-*H*), 6.65 (dd, 2H, furyl-*H*).

2.1.4. Bis(3-(2-furyl)phenyl)diazane (**4**)

Zinc powder (12.0 g, 184 mmol) was added with stirring to (**3**) (6.0 g, 19.0 mmol) in 200 ml acetone under a dried nitrogen atmosphere. Aqueous NH₄Cl solution of 20 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 brown solid was filtered, followed by washing three times with water. The product was dried in vacuum at room temperature for 1 day. The product of 5.8 g was obtained in a yield of 98%; m.p. 121–122°C; ¹H n.m.r. (δ, CDCl₃), 7.44 (t, 2H, furyl-*H*), 7.25–7.18 (m, 6H, Ph-*H*), 6.76 (q, 2H, Ph-*H*), 6.60 (d, 2H, furyl-*H*), 6.44 (dd, 2H, furyl-*H*), 5.66 (s, 2H, NH).

2.1.5. 2,2'-Bis(furyl)benzidine (furylBz)

A mixture of 0.6 g (1.9 mmol) of (**4**) and 30 ml ethanol was stirred under a dried nitrogen atmosphere and then cooled to 0°C using an ice bath. A mixture of 1.5 ml conc. HCl and 10 ml ethanol (95%) was added stepwise to the diazane solution for 1 h. Once the addition was completed, the reaction solution was placed in a refrigerator of *ca.* 4°C for 1 day and, thereafter, filtered. The salt product obtained was converted to the free diamine by treatment with concentrated aqueous sodium hydroxide solution. The

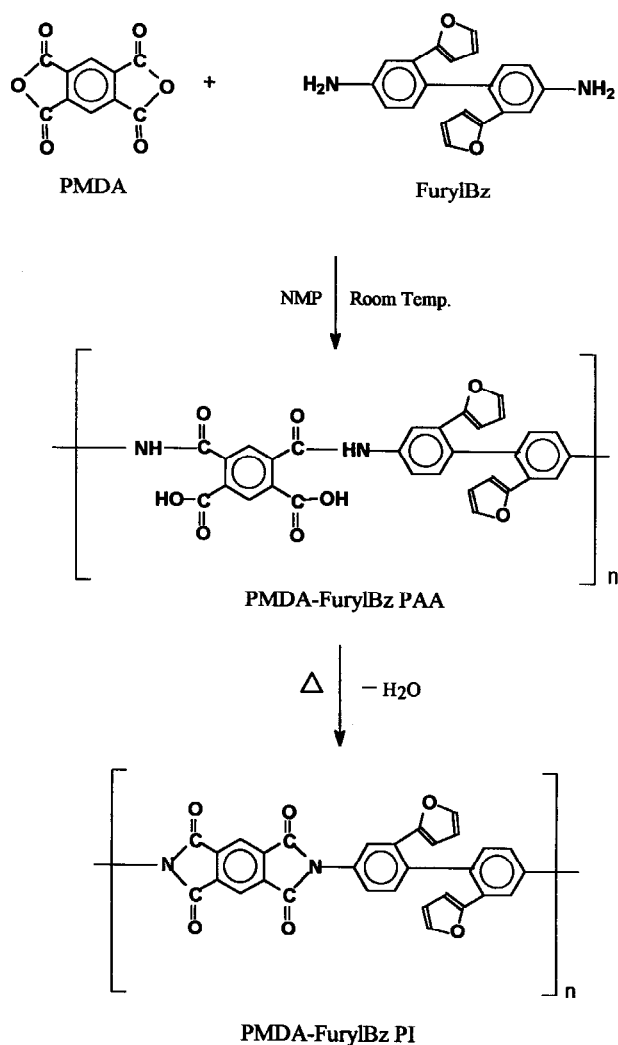


Fig. 2. Synthetic scheme of a soluble poly(amide acid) and its polyimide from 2,2'-bis(furyl)benzidine (FurylBZ) and pyromellitic dianhydride (PMDA).

neutralized filtrate was extracted with chloroform and the main product was separated using a chromatographic column with silica gel and hexane/ethyl acetate/ethanol (6:3:1 in volume) mixture as an eluent solvent. The product separated was further purified by recrystallizing from ethanol/water mixture, followed by drying in vacuum at room temperature for 1 day. The product of 0.12 g was obtained in a yield of 21%: m.p. 156–157°C; ^1H n.m.r. (δ , acetone- d_6), 7.37 (d, 2H, furyl-*H*), 7.25 (d, 2H, Ph-*H*), 6.84 (d, 2H, Ph-*H*), 6.67 (dd, 2H, Ph-*H*), 6.17 (dd, 2H, furyl-*H*), 5.42 (d, 2H, furyl-*H*), 4.78 (s, 4H, NH_2). Elemental anal. calc. for $\text{C}_{20}\text{H}_{16}\text{N}_2$: C, 75.93; H, 5.09; N, 8.85. Found: C, 75.71; H, 4.87; N, 9.50.

2.2. Synthesis of poly(amide acid) and preparation of its polyimide films

Pyromellitic dianhydride (PMDA) purchased from the Chriskev Company was purified by drying at 120°C for

1 day in vacuum prior to use. *N*-Methyl-2-pyrrolidone (NMP) was purified by distillation over calcium hydride under reduced pressure. In a glove box filled with dry nitrogen gas, poly(2,2'-bis(furyl)-4,4'-biphenylene pyromellitimide acid) precursor was prepared by slowly adding 0.6985 g (3.695 mmol) of the purified PMDA to the FurylBZ of 1.1679 g (3.695 mmol) dissolved in 18 ml NMP with stirring vigorously (see Fig. 2). Once the dianhydride addition was completed, the reaction flask was capped tightly and stirring was continued for 1 day to make the polymerization mixture completely homogeneous. The poly(amide acid) solution was filtered with silver metal membranes of 1.0 μm pore size and sealed tightly, stored in a refrigerator of -4°C before use. For the synthesized poly(amide acid), the measurement of intrinsic viscosity $[\eta]$ was carried out in NMP at 25.0°C according to a method described in the literature [16,17]. The value of $[\eta]$ was determined to be 0.545 dl/g.

The poly(amide acid) solution was spin-coated on glass substrates, followed by soft-baking on a hot plate at 80°C for 1 h. The soft-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. A 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 . In addition, for u.v.-visible spectroscopic measurements, polyimide films were prepared on quartz substrates and their thicknesses were in the range of 0.1–2 μm .

2.3. Characterization

Thermogravimetric analysis (t.g.a.) was carried out over 25–800°C for the soft-baked poly(amide acid) and its polyimide using a Perkin-Elmer thermogravimeter under a dry nitrogen gas flow. A ramping rate of 5.0 K/min was employed. Wide-angle X-ray diffraction (WAXD) measurements were also conducted for the polyimide films using a Rigaku diffractometer equipped with a copper target and a scintillation counter.

For FurylBZ monomer and its polyimide, photoluminescent spectra were measured at room temperature using a Shimadzu spectrophotometer with a Xenon lamp. For both excitation and emission monochromators, bandpasses were 2 nm. The new monomer in 1,4-dioxane was excited at 340 nm. The polyimide in films was excited at 380 nm in a front-face arrangement, in order to minimize the self-absorption. The size of polyimide specimens was 10 \times 30 mm. U.v.-visible spectroscopic measurements were performed using a Hewlett-Packard spectrometer. In addition, fluorescence quantum yield (Φ_f) of the new diamine monomer was determined relative to quinine sulfate in 1 N H_2SO_4 at $25 \pm 1^\circ\text{C}$ ($\Phi_f = 0.57$ when excited at 348 nm) [18–20]. That is, the relative quantum yield was obtained by

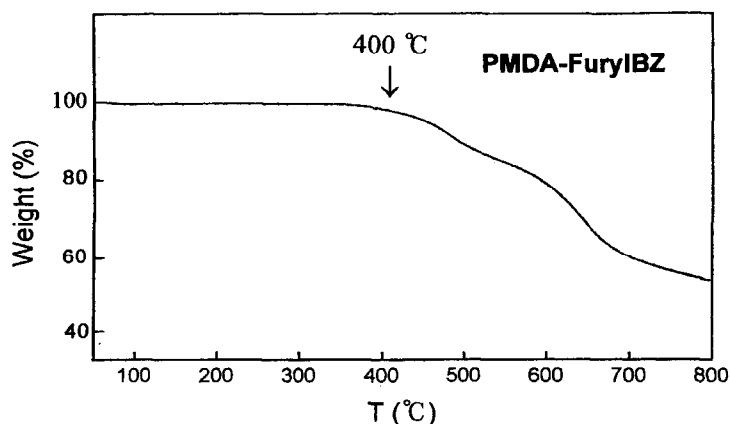


Fig. 3. Thermogravimetric analysis (t.g.a.) of the PMDA-FurylBZ polyimide imidized at 300°C for 1 h. The t.g.a. run was carried out with a ramping rate of 5.0 K/min under a dry nitrogen gas flow.

comparing the ratio of fluorescence emission intensity maximum to u.v. absorbance at the excitation wavelength used for the sample with that of a standard [21]. 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, in order to avoid any inner filter effect. For the polyimide in films, Φ_f was determined by the comparison with *N,N'*-dicyclohexylperylenebisimide dye dispersed in poly(methyl methacrylate) ($\Phi_f = 0.91$) [22]. For each sample quantum yield was measured at least five times and then averaged.

3. Results and discussion

The thermal imidization of PMDA-FurylBZ precursor film was investigated under a dry nitrogen atmosphere by thermogravimetry. In heating run, its weight was drastically dropped up to 300°C, mainly due to the removal of residual NMP solvent as well as byproduct of imidization. Then, the weight loss was leveled off at 300°C. Thus, the precursor was imidized at 300°C for 1 h and then cooled to room temperature. The imidized sample was reheated up to 800°C, in order to investigate its thermal stability. As shown in Fig. 3, the polyimide apparently did not show any weight loss up to ca. 400°C. However, the weight loss was started at ca. 400°C and then gradually increased until ca. 580°C. That is, the thermal stability of this polymer is limited up to ca. 400°C. According to this t.g.a. result, all the polyimide films were prepared by imidizing PMDA-FurylBZ precursor films at 300°C for 1 h.

Morphological information in the polyimide films was obtained by WAXD measurements. The reflection pattern is featureless, showing only a broad amorphous halo. The transmission pattern also exhibited a broad amorphous halo similar to that in the reflection pattern and, furthermore, showed additionally broad peaks: 11.2, 16.7, 33.5, and 44° (2θ). These broad peaks may correspond to the diffraction from the chemical repeat unit of polymer chain in an short-range intermolecular order. Overall, the results indicate that the rod-like polyimide chains are favorably aligned in the film plane rather than randomly, in spite of the poor intermolecular packing due to the bulky furyl side groups.

Fig. 4 shows u.v.-visible absorbance and photoluminescence (PL) behaviors of the FurylBZ monomer with a well-defined conjugation length and its polyimide in films. In the u.v.-visible spectrum, the FurylBZ monomer in 1,4-dioxane exhibits a broad featureless absorption with its low energy edge lying at ca. 326 nm. This absorbance is considered to be the $\pi-\pi^*$ transition, leading to the formation of a singlet exciton. With this u.v.-visible absorbance characteristic, the monomer solution was excited at a wavelength of 340 nm

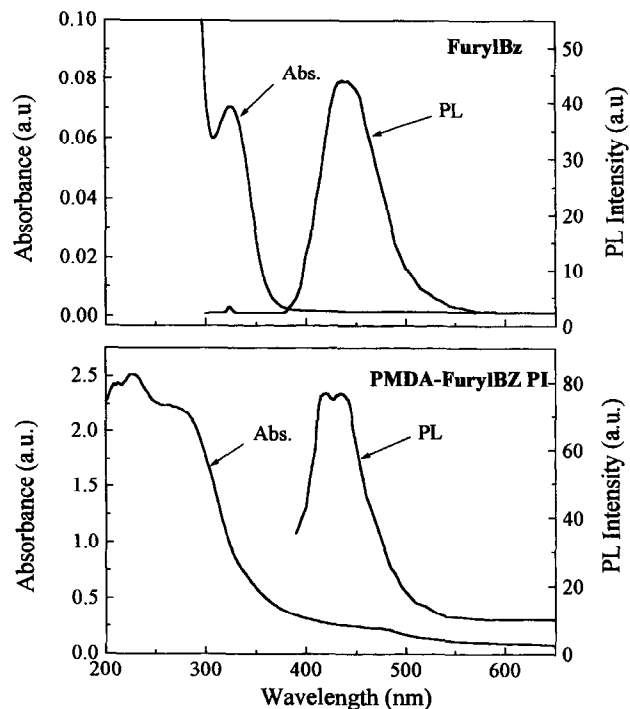


Fig. 4. U.v.-visible absorption and photoluminescence spectra: (top) 2,2'-bis(furyl)benzidine (FurylBZ) dissolved in 1,4-dioxane with a concentration of 1.5×10^{-5} g/ml (the excitation was at 340 nm); (bottom) PMDA-FurylBZ polyimide film imidized at 300°C for 1 h (the excitation was at 380 nm).

which provides the best PL spectrum. The emission spectrum appeared over 373–540 nm, consisting of two emission peaks very close to each other: one peak was centered at 436 nm and the other at 443 nm. The presence of the two peak maxima indicates that the FurylBZ exists possibly in two different types of molecular conformations in which their energy difference is very small. These molecular conformations may be related very closely to the degree of coplanarity between the two phenyl rings of the benzidine backbone, as well as the degree of coplanarity between the phenyl ring of the benzidine backbone and the linked furyl group side group. The emission centered at 443 nm might come from a molecular conformation with higher coplanarities, compared to that at 436 nm. In particular, the emission peak centered at 436 nm is very similar to that of its structural isomer, 5,5'-bis(4-aminophenyl)-2,2'-bifuryl [23]. This might be evidence that the wavelength of PL is mainly dependent upon the effective conjugation length rather than the shape, including linear, kink, and bend shape, in a conjugated molecule. In addition, the full-width at half maximum (FWHM) of the emission spectrum including the two peaks is 67 nm. This broadness is due to the nature of two emission peaks.

On the other hand, the polyimide film also exhibited a broad featureless absorption at less than *ca.* 400 nm. When the film was excited at 380 nm (the maximum excitation wavelength), the emission spectrum was shown to be over the range of 386–545 nm. The spectrum exhibited two peak maxima: one is at 419 and the other at 435 nm. The emission spectrum resembles that of the FurylBZ monomer. In fact, the polyimide consists of two different kinds of chromophores, PMDA and FurylBZ units. However, the fluorescence of the PMDA unit is relatively weak [22,24–28]. Therefore, it is suggested that the PL from the polyimide comes mainly from the FurylBZ chromophore unit. The two emission peaks are also related directly to the polymer chain conformations as well as the morphological structures possible in the solid state film. Otherwise, they may be a vibronic structure. The WAXD patterns indicate that the polyimide in films is amorphous, so that the morphological heterogeneity is expected to be very small. Thus, the two emission peaks might either come from the possible two different conformations of the FurylBZ unit in the polymer backbone or be a vibronic structure. Both of the peaks in the emission spectrum were shifted slightly to the shorter wavelength region, compared to those of the FurylBZ monomer. This may result from either one of the two reasons or both in the following: first, the fluorescence of a chromophore is generally influenced by the nature of a solvent employed to dissolve it, so that the fluorescence of FurylBZ may be changed by varying its solvent; second, the PMDA unit is cooperatively worked out with the linked FurylBZ unit to shift the emission spectrum slightly to the short wavelength region. In addition, for the spectrum, the FWHM is 63 nm, which is relatively broad because of the nature of two emission peaks. However, this FWHM is still relatively

very narrow, compared to those of other light-emitting polymers, such as PPV and its copolymers [1,10–14]. In addition, it is noted here that, for light-emitting polymers, their electroluminescent (EL) spectra are almost identical to the PL spectra. Therefore, an EL spectrum identical to the PL spectrum measured in this study is expected for the PMDA–FurylBZ polyimide.

In addition, relative fluorescence quantum yield (Φ_f) was measured: $\Phi_f = 0.52$ for FurylBZ in dioxane solution and $\Phi_f = 0.074$ for PMDA–FurylBZ polyimide in films. The Φ_f of FurylBZ is relatively lower than those of some *p*-phenylenevinylene derivatives (0.94 for 1,4-bis((4-isopropylphenyl)ethenyl)benzene [11] and 0.8 for 1,4-bis(2,5-dioctylstyryl)benzene [12]), but higher than those of 1,8-diphenyloctatetraene (0.09) [11] and (3-hexylthiophenylene) ethynylene derivatives (0–0.21, depending on the conjugation length) [20]. However, the Φ_f of PMDA–FurylBZ polyimide is comparable to that (0.085–0.115) of poly(2-methoxy-5-(2'-ethyl)hexyloxy-*p*-phenylenevinylene) [29] (that is, an analog of PPV) which emits orange light. Furthermore, the Φ_f is much higher than that (9.7×10^{-7}) of poly(4,4'-oxydiphenylene pyromellitimide) [30] which is the representative of conventional polyimides.

4. Conclusions

A blue light-emitting benzidine derivative, FurylBZ was synthesized and its soluble poly(amide acid) was prepared by the polycondensation with PMDA. The poly(amide acid) was thermally converted to the polyimide in films. The polyimide is thermally stable up to *ca.* 400°C. The polyimide chains in the film are in a short-range order without a regular molecular packing, but aligned favorably in the film plane because of the rod-like chain characteristic. The new FurylBZ monomer exhibited very intense blue light emission with $\Phi_f = 0.52$, whereas its polyimide also emitted intense blue photoluminescence with $\Phi_f = 0.074$. In conclusion, the PMDA–FurylBZ polyimide is a potential candidate material for fabricating optoelectronic devices which can emit blue light.

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