Blue-Light-Emitting Polymers with A Defined Conjugation Length: Effect of Diimide Unit

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Abstract

New light-emitting polyimides were synthesized from the conventional polycondensation of 5,5'-bis(4-aminophenyl)-2,2'-bifuryl (PFDA) with fluorinated and non-fluorinated aromatic dianhydrides, providing a good quality of thin films: 6F-PFDA PI and ODPA-PFDA PI. Their UV-visible absorbance and photoluminescent characteristics were investigated. The polymers emit blue and blue-greenish light in a quantum yield of 7.3-14.9 %, depending on the polymer backbone.

Introduction

Light-emitting polymers have many potential advantages, such as good mechanical and electro-optical properties, various choices of chemical structures, and easy processability in the fabrication of optoelectronic devices. And, a light-emitting device fabricated with poly(*p*-phenylenevinylene) was first demonstrated successfully in 1990 [1]. For these, light-emitting polymeric systems have gained great attention from both academia and industry. In this study, we introduce new blue-light-emitting polyimides based on 5,5'-bis(4-aminophenyl)-2,2'-bifuryl (PFDA) monomer having a well-defined conjugation length.

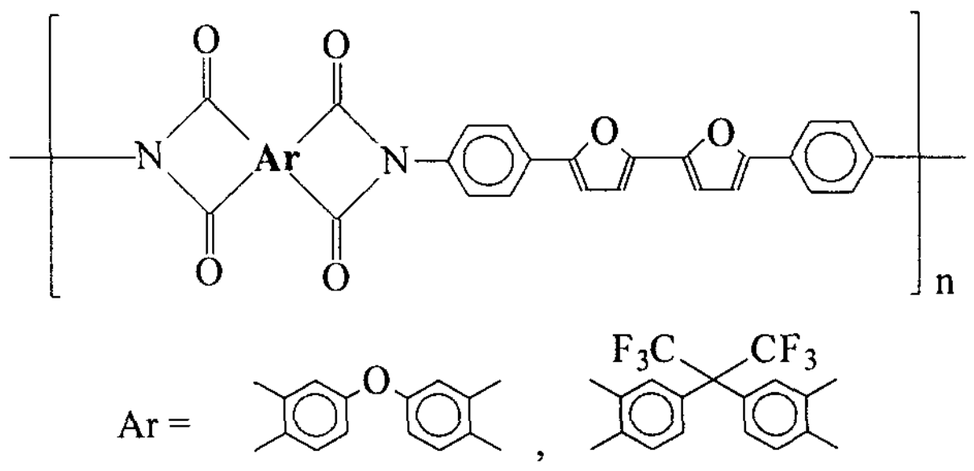

Fig. 1. Chemical structures of light-emitting polyimides (PIs) synthesized in this study: ODPA-PFDA PI and 6F-PFDA PI.

Experimental

PFDA monomer was prepared by a synthetic method reported previously [2]. Adapting a synthetic method of conventional polyimide precursors [2,3], two poly(amic acid) (PAA) precursors were prepared from the polycondensation of PFDA monomer with hexafluoro-isopropylidene-2,2-bisphthalic anhydride (6F) and 4,4'-oxydiphthalic anhydride (ODPA) in dry *N*-methyl-2-pyrrolidone (NMP): 6F-PFDA PAA and ODPA-PFDA PAA. The solid content of each PAA solution was ca. 10 wt %. The PAA solutions were filtered with silver metal membranes of 1.0 μm pore size and sealed tightly, stored in a refrigerator of -4°C before use. For these precursors, the intrinsic viscosity [η] was measured in NMP at 25.0°C as a method described in the literature [2,3].

The PAA solutions were spin-coated on glass and quartz substrates, followed by baking at 80°C for 1 h. The baked PAA films were thermally imidized at 300°C under a dried nitrogen gas flow, giving polyimide (PI) films with a thickness of 10-20 μm (see Fig. 1). The PI films were taken off from the glass substrates, followed by drying for 2 days at 50°C in a vacuum. In addition, for UV-visible spectroscopic measurements, PI films of 0.1-2 μm thickness were prepared on quartz substrates from PAA solutions diluted in a solid content of 1-2 wt %.

For PFDA monomer in 1,4-dioxane and its PIs in films, excitation and photoluminescence spectra were measured at room temperature using a fluorescence spectrophoto-meter (SLM 8000_{TM}) with a Xenon lamp. The excitation wavelength employed was 340 nm for the PFDA solution and 380 nm for the PI films. UV-visible spectroscopic measurements were performed using a Hewlett-Packard spectrometer. In addition, the relative fluorescence quantum yield (Φ_f) was measured in accordance to a method reported previously [3].

Results and Discussion

Two PAA precursor polymers were synthesized with a relatively high molecular weight: [η] was 0.593 dL/g for the 6F-PFDA PAA and 0.634 dL/g for the ODPA-PFDA PAA. These precursors were thermally converted to the corresponding polyimides, giving a good quality of thin polyimide films.

The PFDA exhibits a featureless broad absorption with a maximum at 376 nm which corresponds to the π-π* transition, leading to the formation of a singlet exciton. Its emission spectrum exhibits doublet peaks centered at 415 nm and 440 nm (see Fig. 2). The energy difference between these two peaks is estimated to be very small, that is only 3.9 kcal/mol. These peaks seem to be originated from the *trans*- and *cis*-isomeric structures possible in the PFDA.

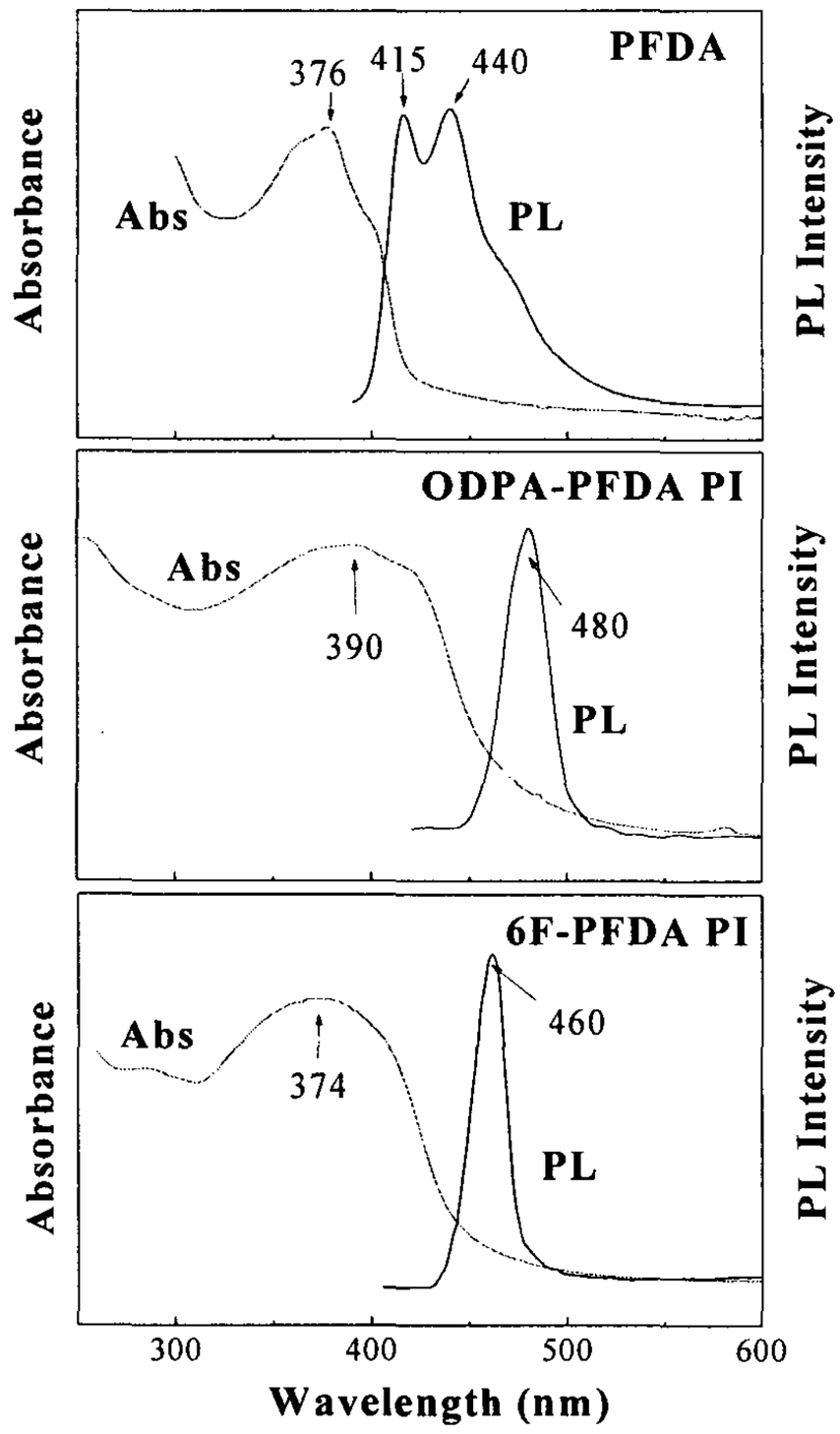

Fig. 2. UV-visible absorbance (Abs) and photoluminescence (PL) spectra of PFDA (1.5 x 10^{-5} g/mL in 1,4-dioxane) and of PIs in thin films. The excitation wavelength was 340 nm for PFDA and 380 nm for PIs.

The PIs in films also exhibit a relatively broad featureless absorption over the range of <466 nm. In general, conventional aromatic polyimides absorb UV-visible light over the range of <470 nm because of the UV absorbance characteristics of aromatic imide rings as well as aromatic rings. This absorbance is overlapped with that of the PFDA, so that the PFDA-based PIs exhibit relatively broader UV-visible spectra than that of the PFDA. When the PIs in films are excited at 380 nm (the maximum excitation wavelength), the strongest emission spectra are obtained. Different from the PFDA, the PIs showed a single emission peak. The peak is centered at 480 nm (blue-greenish light) for the ODPA-PFDA PI and 460 nm (blue light) for the 6F-PFDA PI. These results indicate that the PFDA units in the polymer chain are in a single isomeric state, that is either *cis*-form or *trans*-form.

The emission peaks in the PIs were red-shifted, compared to that of the PFDA. This may be attributed to the electron-withdrawing (or electron-donor) abilities of ODPA and 6F units which can influence the π-π^* transition of PFDA units on the polymer backbone. In addition, the emission peaks are relatively very narrow, compared to that of the PFDA monomer: the full width at half maximum is 26 nm for the ODPA-PFDA PI, 23 nm for the 6F-PFDA PI, and 56 nm for the PFDA. In addition, the PIs exhibited a relatively high quantum yield: Φ_f = 7.3 % for the ODPA-PFDA PI and Φ_f = 14.9 %. These are the unique characteristics of the ODPA-PFDA PI and the 6F-PFDA PI.

Conclusions

New light-emitting polyimides were prepared from the PFDA monomer having a well-defined conjugation length. With a high quantum yield, the 6F-PFDA PI emits blue light, while the ODPA-PFDA PI emits blue-greenish light. These polymers are potential candidate materials for fabricating optoelectronic devices.

Acknowledgments

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