Optical and Electrical Properties of Polyimide Derivatives Including Quinoxaline Moiety

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1. Introduction

Properties of π -conjugated materials is a subject of recent interest of electronic and optical devices.^{1,2,3)} Controlling of the band gap (E_g) is one of the most important factors for their electronic and optical properties. In order to control E_g , introduction of donor / acceptor pair into the same molecule, such as aromatic donor and quinonoid acceptor unit, is one of the promising candidates.^{4,5,6)}

Amino quinoxaline derivatives is one of the key materials to obtain the narrow band gap materials.⁷⁾ In general, these derivatives have a narrow band gap between 2.6 eV to 2.3 eV. The strong fluorescence emission at 550 nm is obtained in the evaporated thin film. In the case of the evaporated film using low molecular materials, morphological stability, however, is not good.

In 1967, Hagenrother, et al. reported to prepare poly(quinoxalines) for heat-resistant adhesives materials for aircraft⁸⁾. Recently, Markus Janke, et al pointed out a light emitting character of poly(phenylquinoxaline). Actually, poly(phenylquinoxaline) film showed excellent emission, at 400-500nm (blue emission)⁹⁾. In order to prepare poly(phenylquinoxaline) derivatives, we have tried electropolymerization⁷⁾. The molecular weight of the obtained polymer, however, was fairly low because of the low solubility of the growing polymer in the solvent. The stable film was, therefore, not obtained by the electropolymerization.

In order to improve the film formation ability,

we paid attention to polyimide homologues containing the quinoxaline unit in the main chain. For this objective, we started to synthesize new diamine monomers containing quinoxaline moiety.

In this paper, we report a synthesis of new diamine derivatives and their polymerization. The optical and electrical properties is also described.

2. Experiment

2.1. Synthesis of Monomers.

The synthetic route of new diamine is described in Scheme 1.

Scheme 1. Synthesis of new diamines.

1,2,3-triaminobenzene was prepared by the reducing reaction of 2,6-dinitroaniline by the use of PdC as reductant. This afforded 1 in a 95% yield.

Bis(phenylaminoquinoxalines) (BPAQs) was prepared by the reaction of 1,2,3-triaminobenzene with 1,4-bisbenzyl in $\text{CH}_3\text{COOH}/\text{MeOH}$ under N_2 conditions. BPAQs (2) was obtained in 90% yield.

2.2. Synthesis of Polyimide (PI).

The synthetic route of polyimide is described in Scheme2. PI was prepared by the reaction of 1,2,4,5-benzenetetracarboxylic dianhydride with BPAQs in anhydrous DMF.

3. Results and Discussion

3.1 Properties of BPAQs.

The optical characterization of BPAQs is shown in Figs.1, 2-1 and 2-2. Energetic level data of the material is listed in Table 1. The HOMO level was measured by the UPS. The Band gap was calculated by the UV-vis spectra.

Scheme 2. Synthesis of Polyimide.

Table 1. Energetic level data of BPAQs.

Compound	HOMO (eV)	LUMO (eV)	Bandgap (eV)
2	6.00	4.27	2.73

Band gap of BPAQs was about 2.7eV. This value is the same as that of 2,3-diphenyl-5-aminoquinoxaline. In spite of the expansion of π -electron, band gap level of BPAQs was not changed. It was thought that benzene ring, as a spacer, did not expand the π -conjugation system of BPAQs because of free rotation bond of 1,4-substituted benzene ring. The fluorescence spectrum is influenced by the concentration of BPAQs. This effect may be attributed to the intermolecular interaction.

Fig. 1 UV-vis spectra of BPAQs in Chloroform solution.
Concentration 10^{-4} mol/l

Fig. 2-1 Normalized fluorescence spectra of BPAQs in chloroform solution.

Fig.2-2 Excitation spectra of BPAQs in chloroform.

●: 10^{-6} mol/l, ○: 10^{-4} mol/l

3.2 Optical properties of polyimide.

Polymerization was carried out in anhydrous DMF at room temperature according to Scheme 2. Measurement of molecular weight of the polymer was carried out the following conditions;

Column: TSK Gel super H3000 (TOSOH)

Eluate: DMF (0.6ml/min ; 3.5MPa)

Result of GPC measurement is as follows;

Mn: 7150, Mn: 9370, Mz:12600

Mz/Mw 1.34, Mw/Mn 1.31

Polyimide thin film (about 100nm) was prepared by the use of spin coating method. An UV-vis spectrum of the polyimide film is shown in Fig.3.

Fig. 3 UV-vis spectra of the polyimide film (Thickness is 300nm)

A fluorescence spectrum of the polyimide film and polyamic acid (DMF varnish) are shown in Fig.4.

Fig.4 Fluorescence spectra of polyimide film and polyamic acid

Fluorescent spectrum of the polyimide film showed ca. 50 nm blue-shift compared to the polyamic acid. Energetic

level data of the polyimide are listed in Table 2. Band Gap level of the polymer was the same as that of BPAQs.

Table 2. Energetic level data of BPAQs

Compound	HOMO (eV)	LUMO (eV)	Band gap (eV)
Polyimide film	6.20	4.40	2.80

3.3 Electrical properties of polyimide.

Current-Voltage curve of the polyimide film is shown in Fig.5. Device structure is as follows;

Glass substrate / ITO / Polyaniline (50nm) / Polyimide (100nm) / Al.

Polyaniline was used as buffer layer because of large HOMO level of polyimide film. Baking of the film was carried out at 130 °C and 220 °C under atmospheric conditions for 30 min. It was observed that current density is depended on the baking temperature of the film. These results suggest the participation of polyamic acid in the film.

Other electric properties of the polymer are under investigation and will be published elsewhere.

Fig.5 Relationship between Current density and Voltage of polyimide film.

Conclusion

Narrow band gap diamines compound having D/A unit (electron-acceptor) was prepared based on quinoxaline unit. Band gap of BPAQs was about 2.7eV. This value was as same as that of 2,3-diphenyl-5-aminoquinoxaline.

The optical properties of polyimide using BPAQs as monomer is almost the same as that of BPAQs. Molecular weight of polyamic acid was about 7000(Mn). Fluorescence spectra of the polyimide film displayed 50nm blue-shift compared to polyamic acid varnish. In the measurement of V-I, it was appeared that the current density is depended on the baking temperature of the polyimide film.

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