

The Fluorescent Effects on the *N*-Substituents of Polyarylenevinylenes Having 1,2-Diphenylmaleimide Moieties

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Abstract: Model compounds and polymers having *N*-substituted 1,2-diphenylmaleimide moieties were synthesized and characterized by NMR, IR, UV, and fluorescence spectroscopy. The fluorescence intensity could be controlled by *N*-substituents of model compounds and polymers. As the structure of an *N*-substituent of them was bulkier, or the electron density of an *N*-substituent was denser, the photoluminescence intensity was increased. All the compounds showed greenish yellow photoluminescence with the maximum intensity between 510 and 537 nm. From quantum efficiency data of the model compounds and the polymers, the fluorescence intensity of the polymer **11** was higher than that of the model compound **4**.

Keywords: *N*-substituted diphenylmaleimide, fluorescence control, quantum efficiency.

Introduction

The fluorescence materials have been studied due to the application to the field of LED, LASER, and biosensor, etc.¹⁻⁴ It is important to understand the fluorescence phenomena themselves, in order to design and prepare new and efficient fluorescent materials. Much of the understanding of the fluorescence has resulted from small organic molecules. The fluorescence of organic molecules has provided information about the symmetry of the molecule, its electronic excited states, and the pathways for dissipation of energy, including the interaction with other molecules.^{5,6} However, it is not clear how the fluorescence was produced. In relation to the molecular structures, many studies have been progressed about the methods of controlling the fluorescence. Through the studies up to now, it has been notified that the two methods of controlling the fluorescence have been known; First, donor-acceptor substituted aromatic compounds have generally highly dipolar charge-separated excited states.⁷ That is, the difference of electron density between a donor and an acceptor exists, and the fluorescent properties concerned with the difference of electron density are explained through a charge transfer concept. Several studies about inter- or intramolecular charge transfer (CT) between amines as electron donors and aromatic rings as acceptors have been done.⁸⁻¹⁴ Second, the presence or absence of the red-shifted CT-fluorescence band induced conformationally

suggests the involvement of intramolecular twisting along the excited state reaction coordinate. This intramolecular twisting is caused by steric hindrance in the molecular structure.¹⁵

In relation to imide-based fluorescent dyes, such as a peryleneimide¹⁶ and a naphthalimide,¹⁷ the effect of *N*-substituents of small imide-molecules on fluorescence has been studied. But it has not been reported on the fluorescent *N*-substituted polymers, which have the π -conjugation.

We report that new fluorescent π -conjugated polymers based on *N*-substituted 1,2-diphenylmaleimide moieties were designed and synthesized. These polymers had good luminescence property and thermal stability, and the fluorescence phenomena were intensively studied.

Experimental

Characterization. Melting points were measured on an Electrothermal IA9100 digital melting point apparatus. ¹H NMR spectra were obtained using a Varian VXR-300 and referenced to tetramethylsilane (TMS). IR spectra were recorded on a Nicolet Avatar 360 FT-IR ESP. Gel permeation chromatography (GPC) was carried out using a Waters GPC system (600S controller, 616 pump, 717 Plus autosampler and 410 differential refractometer), Ultrastyrigel columns in series (Styrigel HR-4, HR-3, HR-1 and HR-5E) and tetrahydrofuran (THF) as the eluent. UV-visible absorption spectra and fluorescence spectra were recorded on a Sincro UVS-2100 and Shimadzu RF 5301PC Spectrofluorophotometer, respectively, using a quartz cuvette.

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Materials. All reagents were purchased from Aldrich, Acros and TCI. Toluene, xylene, triethylamine (Et₃N) and methylenechloride were distilled over calcium hydride. 2,2-Bipyridyl (bpy) was used after recrystallization from ethanol. Triphenylphosphine (PPh₃) was used after recrystallization from hexane and then ethanol in twice. 3,4-Bisphenyl-3-cyclobutene-1,2-dione and 3,4-bisphenyl-2,5-furanedione^{18,19} were prepared according to the previously reported procedure. Other reagents were used without further purification.

Synthesis of Model Compounds.

3,4-Bisphenyl-*N*-phenyl-pyrrole-2,5-dione (1): The mixture of 3,4-bisphenyl-2,5-furanedione (0.75 g, 3 mmol), aniline (0.30 g, 3.2 mmol) and Et₃N (catalytic amount: 7 drop) in toluene (40 mL) was refluxed for 24 h. Water was removed using a Dean-Stark trap. Then toluene was removed using an evaporator under a reduced pressure. The yellow product was obtained after recrystallization from ethanol. Compounds **1-6** were synthesized through the same method.²⁰

Yield: 0.77 g (79%), m.p. 165 °C. ¹H NMR (CDCl₃): δ = 7.55-7.25 (aromatic CH). IR (KBr): 3056 (aromatic CH), 1763 (sym. C=O) and 1710 (asym. C=O), 1382 cm⁻¹ (C-N).

3,4-Bisphenyl-*N*-2-methyl-phenyl-pyrrole-2,5-dione (2): Yield: 0.42 g (42%), m.p. 167 °C. ¹H NMR (CDCl₃): δ = 7.6-7.3 (aromatic CH), 2.1 (CH₃). IR (KBr): 3044 (aromatic CH), 2986 and 2912 (aliphatic CH), 1766 (sym. C=O) and 1707 (asym. C=O), 1375 cm⁻¹ (C-N).

3,4-Bisphenyl-*N*-2,6-dimethyl-phenyl-pyrrole-2,5-dione (3): Yield: 1 g (47%), m.p. 190 °C. ¹H NMR (CDCl₃): δ = 7.6-7.3 (H¹⁰ aromatic CH), 7.2-7.1 (H³ aromatic CH), 2.1 (CH₃). IR (KBr): 3064 (aromatic CH), 2978 and 2924 (aliphatic CH), 1763 (sym. C=O) and 1706 (asym. C=O), 1371 cm⁻¹ (C-N).

3,4-Bisphenyl-*N*-2,6-diisopropyl-phenyl-pyrrole-2,5-dione (4): Yield: 0.32 g (26%), m.p. 195 °C. ¹H NMR (CDCl₃): δ = 7.6-7.35 (aromatic CH), 2.8 (-CH-), 1.2 (CH₃). IR (KBr): 3064 (aromatic CH), 2966 and 2866 (aliphatic CH), 1817 (sym. C=O) and 1757 (asym. C=O), 1353 cm⁻¹ (C-N).

3,4-Bisphenyl-*N*-4-nitrophenyl-pyrrole-2,5-dione (5): Yield: 0.39 g (53%), m.p. 170 °C. ¹H NMR (CDCl₃): δ = 8.4 and 7.8 (H⁴ aromatic CH), 7.6-7.35 (H¹⁰ aromatic CH). IR (KBr): 3060 (aromatic CH), 1760 (sym. C=O) and 1710 (asym. C=O), 1345 cm⁻¹ (C-N).

3,4-Bisphenyl-*N*-4-pyridyl-pyrrole-2,5-dione (6): Yield: 0.26 g (42%), m.p. 196-198 °C. ¹H NMR (CDCl₃): δ = 8.75 and 7.65 (H⁴ aromatic CH), 7.55-7.35 (H¹⁰ aromatic CH). IR (KBr): 3060 and 3025 (aromatic CH), 1759 (sym. C=O) and 1711 (asym. C=O), 1389 cm⁻¹ (C-N).

3,4-Bisphenyl-*N*-pentafluorophenyl-pyrrole-2,5-dione (7): The mixture of 3,4-bisphenyl-2,5-furanedione (0.5 g, 2 mmol), pentafluoroaniline (0.37 g, 2 mmol) in toluene (5 mL) was stirred for 30 min. Then tributylamine (0.5 mL) and xylene (15 mL) were added. The mixture was refluxed using a Dean-Stark trap for 12 h. Then xylene was almost removed, and acetic acid (30 mL) was added. The mixture

was refluxed at 130-140 °C for 16 h and then vaporized to make a thick solution. Acetic acid (40 mL) was added one more time, and refluxed. After 3 days, xylene was added and then refluxed for 1 day. Then solvents were removed using an evaporator under reduced pressure. The thick yellow product was obtained after recrystallization from hot chloroform and methanol.

Yield: 0.18 g (21.5%), m.p. 160 °C. ¹H NMR (CDCl₃): δ = 7.6-7.35 (aromatic CH). IR (KBr): 3056 (aromatic CH), 1760 (sym. C=O) and 1724 (asym. C=O), 1360 cm⁻¹ (C-N).

Synthesis of Monomers.

3,4-Bis(4-bromophenyl)-*N*-phenyl-pyrrole-2,5-dione (8): Monomers **8** and **9** were prepared through the same method described for the compound **1** using bromobenzene instead of benzene.

Yield: 1.24 g (87%), m.p. 180 °C. ¹H NMR (CDCl₃): δ = 7.6-7.25 (aromatic CH). IR (KBr): 3079 (aromatic CH), 1763 and 1706 (C=O), 1374 (C-N), 1068 and 1009 cm⁻¹ (C-Br).

3,4-Bis(4-bromophenyl)-*N*-2,6-isopropyl-phenyl-pyrrole-2,5-dione (9): Yield: 1.43 g (87%), m.p. 250 °C. ¹H NMR (CDCl₃): δ = 7.6-7.3 (aromatic CH), 2.7 (-CH-), 1.2 (CH₃). IR (KBr): 3064 (aromatic CH), 2959 and 2866 (aliphatic CH), 1725 and 1707 (C=O), 1353 (C-N), 1085 and 1006 cm⁻¹ (C-Br).

Synthesis of Polymers.

Poly(3,4-bisphenyl-*N*-phenyl-pyrrole-2,5-dione) (10): Zn (0.098 g, 1.5 mmol), PPh₃ (0.131 g, 0.5 mmol), bpy (0.00586 g, 0.0375 mmol), NiCl₂ (0.00486 g, 0.0375 mmol), and monomer **8** (0.24 g, 0.5 mmol) under an argon atmosphere were placed in a 20 mL sealed vial. Dry DMF (0.3 mL) was added using a syringe through a rubber septum. The mixture was stirred at 90 °C under a nitrogen atmosphere for 36 h. Then, DMF (0.5 mL) was added and the mixture was stirred for 0.5 h. The resultant mixture was poured into the mixture of methanol (180 mL) and concentrated HCl (20 mL). Precipitated yellow polymer **10** was collected, washed with warm methanol, water, and ethanol and then, dried *in vacuo* at 40 °C.²¹

Yield: 0.1 g, ¹H NMR (CDCl₃): δ = 7.8-7.3 (aromatic CH). IR (KBr): 3029 (aromatic CH), 1770 and 1712 (C=O), 1386 cm⁻¹ (C-N).

Poly(3,4-bisphenyl-*N*-2,6-diisopropyl-phenyl-pyrrole-2,5-dione) (11): Polymer **11** was prepared using the same procedure described for polymer **10** previously. Yield: 0.12 g, ¹H NMR (CDCl₃): δ = 7.6-7.3 (aromatic CH), 2.8-2.7 (-CH-), 1.2 (CH₃). IR (KBr): 3067 (aromatic CH), 2963 and 2866 (aliphatic CH), 1766 and 1711 (C=O), 1378 cm⁻¹ (C-N).

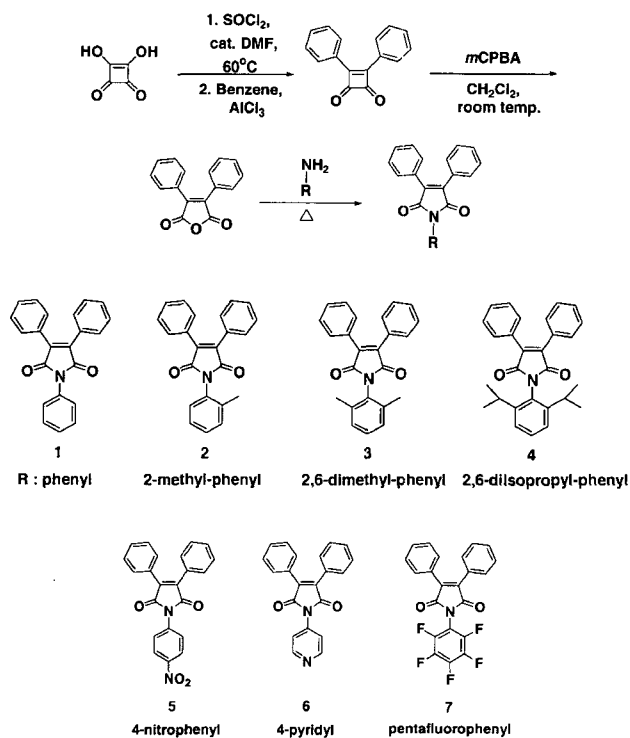
Results and Discussion

Synthesis of the Model Compounds, the Monomers and the Polymers. 3,4-Bisphenyl-2,5-furanedione was prepared through 3 steps. The key reaction was a Beayer-Villiger-type mild oxidation that was reported by Maahs *et al.* and Blomquist *et al.*^{19,22} The first step was to prepare squaryl dichlo-

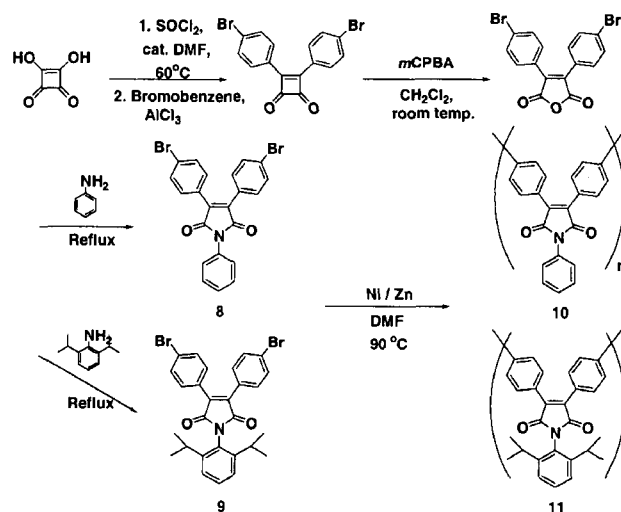
ride using the chlorination of squaric acid with SOCl_2 . Then the Friedel-Craft-type acylation of squaryl dichloride with benzene produced 3,4-bisphenyl-3-cyclo-butene-1,2-dione. To prepare 1,2-diphenylmaleic anhydride, *m*CPBA and CH_2Cl_2 were used as an oxidizing reagent and a solvent. *m*CPBA could prevent hydrolysis of the resulting anhydride product.^{18,23} Oxidation of the 1,2-dione **1** provided fluorescent 3,4-bisphenyl-2,5-furanedione.

Using the thermal imidization of the diphenylmaleic anhydride, seven kinds of model compounds were synthesized (Scheme I). They were prepared by the same imidization methods except for 3,4-bisphenyl-*N*-pentafluorophenyl-pyrrole-2,5-dione (**7**). The diphenylmaleimide, 3,4-bisphenyl-*N*-phenyl-pyrrole-2,5-dione (**1**), was provided by the thermal imidization of 3,4-bisphenyl-2,5-furanedione with aniline in toluene quantitatively. In case of 3,4-bisphenyl-*N*-pentafluorophenyl-pyrrole-2,5-dione (**7**), due to the poor solubility of pentafluoroaniline in toluene, xylene and benzene, acetic acid was used as a main solvent and the reaction was carried out for 4 days with the reflux.

3,4-Bis(4-bromophenyl)-*N*-phenyl-pyrrole-2,5-dione (**8**) and 3,4-bis(4-bromophenyl)-*N*-2,6-isopropyl-phenyl-pyrrole-2,5-dione (**9**) were prepared using the same procedure described for the compound **1**. Yamamoto *et al.* reported on the synthesis of polymers by the nickel-catalyzed coupling polymerization of aryl dihalides in the presence of zinc.²⁴ Dehalogenation polycondensation of the monomers **8** and **9**



Scheme I. Synthesis of the model compounds based on the *N*-substituted diphenylmaleimides.



Scheme II. Synthesis of the monomers **8-9** and the polymers **10-11**.

by the use of a zerovalent nickel complex gave the π -conjugated polymers **10** and **11**. Scheme II showed the procedure of the monomers and the polymers syntheses. The polymers **10** and **11** showed good solubility in most common organic solvents, such as chloroform, THF and DMF.

Characterization of the Model Compounds, the Monomers and the Polymers.

Microstructural Characterization: The characteristic stretching absorption band of anhydride at 1269 cm^{-1} , which was not shown in the IR spectrum of 3,4-bisphenyl-3-cyclobutane-1,2-dione, was detected in the IR spectrum of 3,4-bisphenyl-2,5-furanedione. ^1H NMR spectrum of 3,4-bisphenyl-3-cyclobutane-1,2-dione showed the aromatic proton peak between δ 7.3 and δ 7.7 ppm.

The IR spectrum of 3,4-bisphenyl-*N*-phenyl-pyrrole-2,5-dione (**1**) showed the characteristic imide group absorption bands of symmetric C=O stretching band at 1763 cm^{-1} , asymmetric C=O stretching band at 1710 cm^{-1} and C-N stretching band at 1382 cm^{-1} . The ^1H -NMR spectrum (Figure 1) showed that the model compound **1** had the well-defined as the expected structure. The IR spectra of other diphenylmaleimides showed the similar forms of the characteristic imide group. At the ^1H NMR spectrum of 3,4-bisphenyl-*N*-2-methyl-phenyl-pyrrole-2,5-dione (**2**), the methyl protons in an aliphatic chain were found at $\delta = 2.1$ ppm. In case of the compound **4**, the methylene protons in an aliphatic chain were found at $\delta = 2.8$ ppm and the methyl protons at $\delta = 1.2$ ppm. In case of the compounds **5** and **6**, the proton peak adjacent to the nitrogen was shifted to downfield due to the electron withdrawing effect of the nitrogen. Ten aromatic protons of all compounds were found between $\delta = 7.6$ and $\delta = 7.3$ ppm.

The characteristic stretching bands of aryl bromide at 1068 cm^{-1} , shown in the IR spectrum of the monomer **8**, and

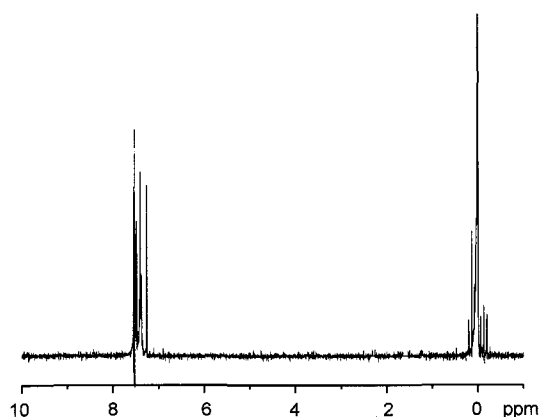


Figure 1. ^1H NMR spectrum of the model compound **1**.

at 1085 cm^{-1} , shown in that of the monomer **9**, almost disappeared in the IR spectrum of the polymers **10** and **11**. The weight-average molecular weight (M_w) of the polymer **10** was determined to be 3,796 with a polydispersity index (M_w/M_n) of 1.8. In case of the polymer **11**, M_w was determined to be 3,260 with a polydispersity index of 1.45. Polymers showed good film formability in spite of their low molecular weights.

Optical Properties: The absorption spectra and the photoluminescence spectra of the model compounds in chloroform solutions at a concentration of $1 \times 10^{-6}\text{ M}$ were shown in Figures 2 and 3. The absorption maxima of all compounds were detected between 348 and 373 nm. When all of the compounds were excited at 365 nm, they showed the greenish yellow fluorescence with the maximum intensity at 510 nm. The photoluminescence properties of the model compounds showed the differences according to the *N*-substituents. As shown in Figures 2 and 3, the bulkier the structure of the *N*-substituent (the effect of the steric hindrance) was or the denser the electron density of *N*-substituent (the effect of the electron density) was, the higher the photoluminescence spectrum was. The compounds **1** through **4** were designed to show the steric effect according to the *N*-substituents. In Figure 2 and Table I, the fluorescence of the compound **1** was hardly observed, but the compound **4** showed the high fluorescence intensity. This fact indicated that the bulkiness of the *N*-substituent affected the fluorescence intensity of these compounds. As represented in Figure 3 and Table I, the compounds **1**, **5**, **6**, and **7** exhibited that the electron density of the *N*-substituents affected the fluorescence of the compounds. The fluorescence intensity of the compounds **6** and **7** was very high, but the compound **5** showed very low fluorescence intensity due to quenching by a nitro group of the *N*-substituent.²⁵

The polymers **10** and **11** were studied about the steric effect of the *N*-substituents. Figure 4 showed the normalized UV-visible absorption and the fluorescence spectra of the

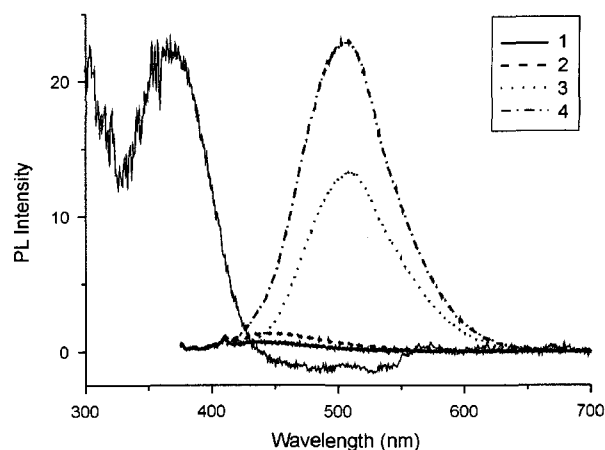


Figure 2. Normalized optical absorption and photoluminescence spectra of model compounds **1-4** in chloroform solution ($1 \times 10^{-6}\text{ M}$): The effect of the steric hindrance.

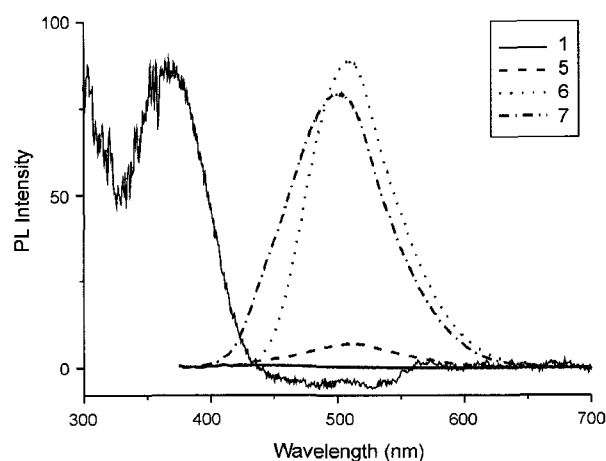


Figure 3. Normalized optical absorption and photoluminescence spectra of model compounds **1, 5, 6, and 7** in chloroform solution ($1 \times 10^{-6}\text{ M}$): The effect of the electron density.

Table I. Quantum Efficiency Ratio of the Model Compounds 1-7 and the Polymers 10-11

	Quantum Efficiency Ratio
Compound 1	0.299
Compound 2	0.99
Compound 3	4.10
Compound 4	16.42
Compound 5	3.69
Compound 6	66.04
Compound 7	39.18
Compound 10	1.27
Compound 11	100

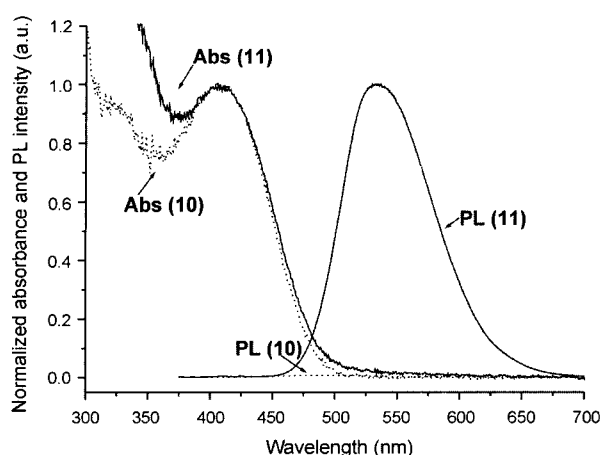


Figure 4. Normalized optical absorption (Abs) and photoluminescence (PL) spectra of the polymers **10** and **11** in chloroform solution (1×10^{-6} M).

polymers **10** and **11** in chloroform solutions at a concentration of 1×10^{-6} M. The maximum absorption wavelength of the polymers **10** (406 nm) and **11** (412 nm) was shifted to the red region relative to that of the model compounds **1** (373 nm) and **4** (365 nm) due to the extension of π -conjugation of the polymers. The photoluminescence was hardly detected in the model compound **1** and the polymer **10**. The photoluminescence spectrum of the polymer **11** with the maximum intensity at 537 nm was also red-shifted up to 29 nm in comparison with that of the compound **4** (508 nm).¹⁸

From the analysis of optical absorbance and integration of luminescence,²⁶ the quantum efficiency was determined. Relative fluorescence quantum efficiencies were determined according to the following relationship (1)

$$\phi_F = \phi_{F,ref} (A_{ref}/A) (n_D/n_{D,ref})^2 (a/a_{ref}) \quad (1)$$

where $\phi_{F,ref}$ is the fluorescence quantum efficiency of a reference compound, A the absorbance, n_D the index of refraction of the solvent, and a the area under the fluorescence peak. This expression is only valid, however, assuming that the relationships between absorbance and concentration and the area under the fluorescence peak and concentration are linear.²⁷ Table I showed the quantum efficiency ratio of the model compounds and the polymers. According to N -substituents from the compounds **1** to **4**, the differences of relative quantum efficiency were showed. From Table I, the compound **4** showed 4 times higher quantum efficiency than the compound **3**, and 16 times higher quantum efficiency than the compound **2**. These results exhibited that the fluorescence intensity was influenced by the steric hindrance of N -substituents. The compound **6** showed 4 times higher quantum efficiency than the compound **4**. Especially, the quantum efficiency of the polymer **11** was 4 times higher than that of the compound **4**. From these results, it is confirmed

that the electron density was more effective than the steric hindrance in our compounds, and the fluorescence intensity increased after the polymerization.

From the fluorescence and the quantum efficiency data, the diphenylmaleimide moiety having the bulkier N -substituent and having the electron withdrawing group showed higher photoluminescence intensity.

In conclusion, we confirmed that the fluorescent properties of the N -substituted model compounds and polymers could be controlled by the steric hindrance according to the bulkiness of N -substituents and the difference of the electron density through the results.

Conclusions

We have synthesized and characterized 1,2-diphenylmaleimide-type model compounds **1-7**, and the π -conjugated polymers **10** and **11**. The polymers **10** and **11** were prepared by a zerovalent Ni complex-mediated dehalogenation polymerization. The weight-average molecular weight (\overline{M}_w) of the polymer **10** was determined to be 3,796 with a polydispersity index ($\overline{M}_w/\overline{M}_n$) of 1.8. In case of the polymer **11**, \overline{M}_w was determined to be 3,260 with a polydispersity index of 1.45. These polymers showed good solubility in common organic solvents such as chloroform, toluene, benzene. And the film formability of the polymers was good. The model compounds showed the greenish yellow photoluminescence with the maxima at 510 nm in a chloroform solution. As the structures of N -substituents in our compounds were bulkier, or the electron density of N -substituents was denser, the photoluminescence intensity was higher. After the polymerization progressed, the photoluminescence intensity was also higher. In case of the compound **5** that has a quencher, a nitro group, the photoluminescence intensity was very low. The polymer **11** also showed greenish yellow photoluminescence. However, the maximum intensity of the polymer **11** was observed at 537 nm relative to that of the model compound **4**. From the analysis of optical absorbance and the integration of luminescence, the quantum efficiency was determined.

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