ELSEVIER

Dyes and Pigments 52 (2002) 37–45

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Synthesis and properties of violet light-emitting polymeric fluorophore

Chil-Won Lee[a], Sang-Woo Joo[a], Ohyoung Kim[b], Jaejung Ko[c],
Myoung-Seon Gong[a,]*

[a]*Department of Chemistry, Dankook University, Cheonan, Chungnam 330-714, South Korea*
[b]*Department of Polymer Science and Engineering, Dankook University, Seoul 140-714, South Korea*
[c]*Department of Chemistry, Korea University, Chochiwon, Chungnam 339-700, South Korea*

Received 24 July 2001; received in revised form 8 August 2001; accepted 6 September 2001

Abstract

Chemiluminescent violet light-emitting polymeric fluorophores were synthesized by copolycondensation of *N,N′*-dihydroxypropyl-1,6,7,12-tetrakis(*p-tert*-butylphenoxy)-3,4,910-perylene tetracarboxydiimide and 2-chloro-9,10-di(*p*-hydroxyphenyl)anthracene with sebacoyl chloride and hexamethylene diisocyanate. The properties of fluorophore polymers were studied by absorption and photoluminescent spectroscopies. The intensities of UV–vis absorbance and photoluminescence spectra appeared at the blue side and the red side of the spectral region. Peroxyoxalate chemiluminescence of polymers provided a strong chemiluminescent violet light emission according to the content of two chromophore units; these were similar to the photoluminescent spectra. © 2002 Published by Elsevier Science Ltd.

Keywords: Perylene tetracarboxydiimide; Diphenyl anthracene; Violet light; Chemiluminescence; Polymeric fluorophore; Color mixing; Copolymerization

1. Introduction

The reactions of aryloxalates with hydrogen peroxide are applied in chemical light stick system [1,2]. Recently chemiluminescence reactions have stirred up a great deal interest in the last few years, as they can offer a unique and sensitive means for analyzing molecules at very low concentrations and compete, in sensitivity, even with the classical radiometric methods [3,4]. Conventional fluorophores used in conjunction with chemiluminescent molecules are highly conjugated aromatic compounds such as 2-chloro-9,10-di(*p*-methoxyphenyl)-anthracene, 9,10-bis(phenylethynyl)anthracene derivatives and *N,N′*-bis(2,6-diisopropylphenyl)-1,6,7,12-tetrakis(*p-tert*-butylphenoxy)-3,4,9,10-perylene tetracarboxydiimide [5,6]. However, for many analytical applications are required in variety solvents, the use of these groups of dyes is limited due to the insolubility in various solvents. Although the chemical light stick system required tuned variety colors, the available colors were limited only to red, blue and yellow green without mixing of fluorophores. It was therefore suggested to overcome this problem by using copolymerization of monomers containing chromophore moiety.

---

* Corresponding author. Fax: +82-41-551-9229.
E-mail address: msgong@anseo.dankook.ac.kr
(M.-S. Gong).

PII: S0143-7208(01)00062-6

The commercially available chemiluminescent light devices or system fail to prevent pollution of fluorophore after finishing the glow of a light source. A particular class of fluorophores of interest is the polymeric fluorophores, which are generally more tractable and stable than conventional molecular fluorophores. Surprisingly, only very few reports have been published on the polymeric chemiluminescent fluorophores [7–10].

In this report, perylenetetracarboxylic diimide- and 2-chloro-9,10-diphenyl anthracene-containing polymeric fluorophores were prepared to emit violet colors according to the composition of copolymer. Their chemiluminescent characteristics including various optical properties were also examined.

2. Experimental

2.1. Chemicals and instruments

N,N′-Dihydroxypropyl-1,6,7,12-tetrakis(*p*-*tert*-butylphenoxy) - 3,4,910 - perylene tetracarboxydiimide [11], 2 - chloro - 9,10 - di*(p* - hydroxyphenyl)anthracene and bis(2 - carbopentyloxy - 3,5,6 - trichlorophenyl)oxalate (CPPO) [12] were prepared by the method previously reported. Sebacoyl chloride, hexamethylene diisocyanate sodium salicylate, pinacol, dibutylphthalate (GR, Yakuri Co.) and dimethylphthalate (GR, Junsei Chem. Co.) were used without further purification. Hydrogen peroxide (35%) was concentrated by using anhydrous magnesium sulfate prior to use. FT–IR spectra were obtained with a Midac Model M-1200 spectrophotometer and ^{1}H NMR spectra were recorded on a Varian Gemini-2000 spectrometer. UV spectra were obtained on a Shimadzu model UV-2100S spectrophotometer. Gel-permeation chromatography (GPC) data were obtained with a Waters HPLC using three columns (μ-Stryragel 10^2, 10^3 and 10^4 Å) in THF and calibrated with polystyrene standards at 20 °C. Intrinsic viscosity of polymer solutions was measured in a Ubbelode viscometer at 25 °C in dibutylphthalate. Intensity of the emission light was measured with a Minolta Chromameter CS-l00. Photoluminescence were measured on an Optical Spectra Multichannel Analyzer (OSMA-1000, Photodiodes 1024).

2.2. Representative preparation of polyester or polyurethane containing perylene or diphenylanthracene units

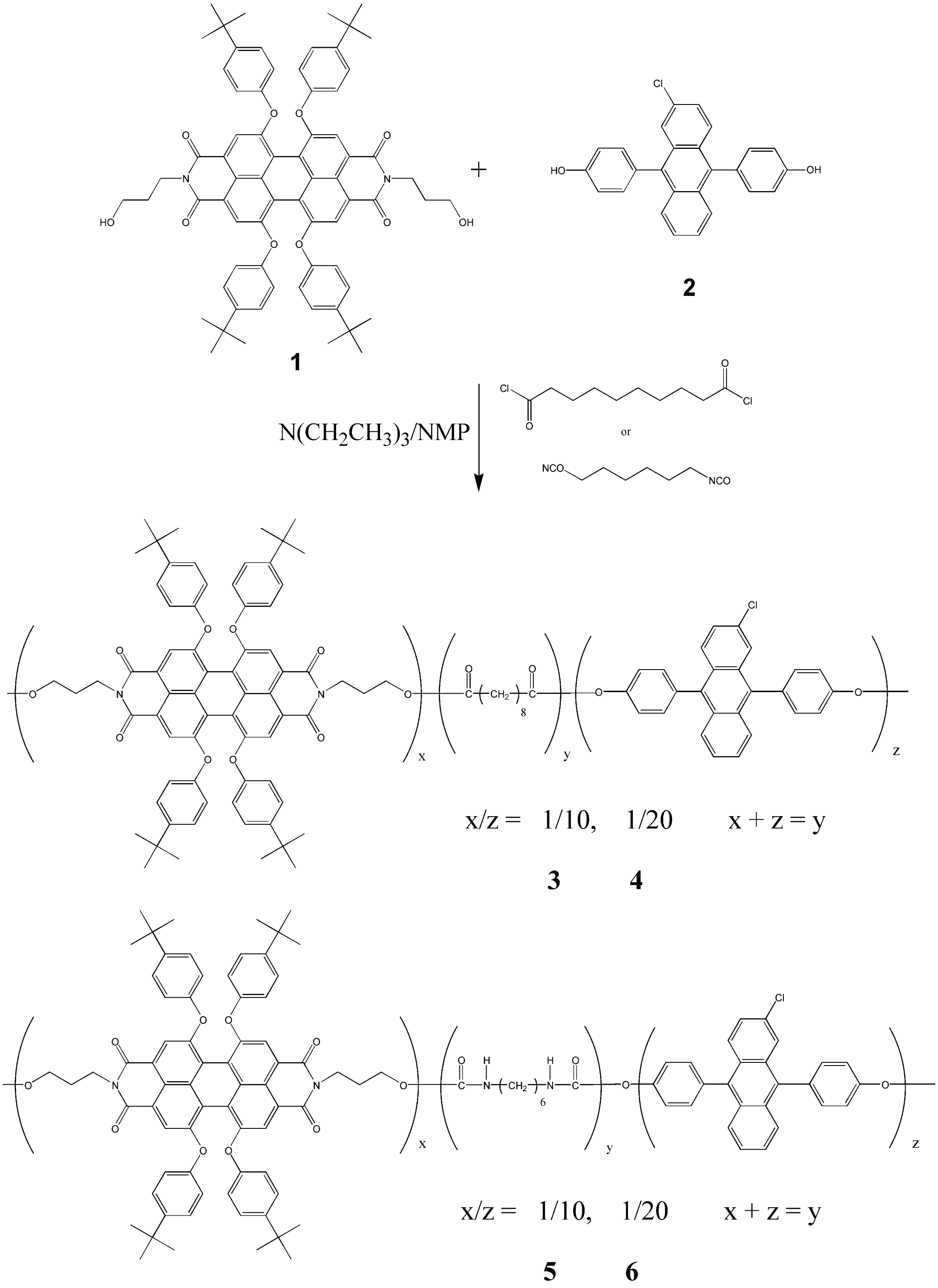
A solution of **1** (1.96 g, 1.8 mol), **2** (8.1 g, 18 mol) and triethylamine (4.55 g, 45 mmol) dissolved in NMP (80 ml) was placed in a three necked flask equipped with a dropping funnel and a nitrogen inlet. After a mixture of sebacoyl chloride (4.75 g, 19.8 mmol) in NMP (30 ml) was added to the reaction mixture for 1 h at 0 °C with vigorous stirring. The temperature was raised to 80 °C and maintained for 15 h. The dark red solution was allowed to cool and poured into distilled water to precipitate the polymer. The solid precipitate was filtered and dried under vacuum at 60 °C for 12 h to give polymer **3** with a yield of 91%. Other copolymer **4** was prepared by the similar method. Polyurethanes **5** and **6** containing red and blue chromophore were also prepared by reacting **1** or **2** with hexamethylene diisocyanate using similar method except catalytic amount of triethylamine.

3: Yield 91%. FT–IR (KBr): 3080–3010 (aromatic C–H), 2940–2880 (aliphatic C–H), 1742 (*s*, ester C=O), 1659, 1698 (*w*, diimide C=O), 1250–1050 (*s*, C–O and C–N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.22 (*s*, 4H, perylene), 7.70 (*m*, 8H, anthracene) 7.22, 6.81 (2 *m*, 25H, phenyl), 4.28 (*t*, 4H, 4–CH_2–O–CO–), 3.68 (*t*, 4H, 2–O–CH_2–), 3.58 (*t*, 4H, =N–CH_2–), 2.45 (*m*, 4H, 2–O–CO–CH_2–), 1.97 (*m*, 4H, 2–CH_2–), 1.52 (*m*, 12H, –$(CH_2)_6$–), 1.28 (*s*, 36H, 4 –$C(CH_3)_3$).

5: Yield 91%. FT-IR (KBr): 3400 (N–H), 3080–3010 (aromatic C–H), 2940–2880 (*s*, aliphatic C–H), 1715 (*s*, urethane C=O), 1659, 1698 (*w*, diimide C=O), 1250–1050 (*s*, C–O and C–N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.22 (*s*, 4H, perylene), 7.70 (*m*, 8H, anthracene) 7.22, 6.81 (2 *m*, 25H, phenyl), 4.42 (*br*, 2H, 2–NH–), 4.28 (*t*, 8H, 4–CH_2–O–CO–), 3.68 (*t*, 4H, 2–O–CH_2–), 3.58 (*t*, 4H, =N–CH_2–), 3.25 (*m*, 4H, 2–O–CO–NH–CH_2–), 1.97 (*m*, 4H, 2–CH_2–), 1.52 (*m*, 8H, –$(CH_2)_4$–), 1.28 (*s*, 36H, 4–$C(CH_3)_3$).

2.3. Examination of the chemiluminescent property

Polymeric fluorophore **3** (0.3 wt.%) and bis(2-carbopentyloxy-3,5,6-trichlorophenyl)oxalate (CPPO, 20 mmol) were dissolved in dibutylphthalate (20 ml)


HO
OH
N
O
Cl
1
2
N(CH2CH3)3/NMP
Cl
O
or
NCO
NCO
CH2
8
x
y
z
x/z = 1/10, 1/20 x + z = y
3 4
H
CH2
6
x
y
z
x/z = 1/10, 1/20 x + z = y
5 6

Scheme 1.

at 80 °C under nitrogen. On the other hand, hydrogen peroxide (90%, 1.5 equivalent of CPPO) and sodium salicylate (0.25 mmol) were dissolved in 20 ml of mixed solvent of dimethylphthalate/pinacol (3/2).

Rates of catalytic decomposition of CPPO were determined by monitoring the decay intensity of chemiluminescent fluorophore solutions. A cylindrical polypropylene tube (I.D., 4 mm; L, 50 mm) was filled with hydrogen peroxide solution (0.3 ml) and a glass capillary containing fluorophore solution (0.9 ml), and sealed with a melted polypropylene. The sample was bent to break and placed in the thermostatic sample block of the chemiluminescence-measuring luminometer. Measurement of the signal was begun by opening the shutter and the chemiluminescent decay was generally recorded.

3. Results and discussion

3.1. Synthesis of copolyester containing red and blue chromophores

The red fluorophore monomer, *N,N′*-bis(3-hydroxypropyl)-1,6,7,12-tetrakis(*p-tert*-butylphenoxy)-3,4,910-perylenetetracarboxydiimide (**1**) was prepared from *N,N′*-dihydroxypropyl-1,6,7,12-tetrachloro-3,4,9,10-perylenetetracarboxydiimide and *p-tert*-butylphenol [11]. The blue fluorophore monomer, 2-chloro-9,10-di(*p*-hydroxyphenyl)anthracene was prepared by acid ether cleavage reaction of 2-chloro-9,10-di(*p*-methoxyphenyl)anthracene with hydrobromic acid in acetic acid solution [13].

Copolyester fluorophores containing red and blue chromophore unit were prepared from **1**, **2** and sebacoyl chloride or hexamethylene diisocyanate in the following mole ratio: **1**/**2** = 1/10 and 1/20 as shown in Scheme 1. Since the reactivity of primary alcohol in **1** and aromatic alcohol in **2** to acid chloride is different because of different pK_a. It has possibility that the acid chloride and isocyanate may be attacked by two **1** and two **2**. Therefore the composition of polymer may be different from the monomer feed ratio. But the polymers were obtained in high yield.

3.2. Properties of polymeric dyes

Table 1 summarizes the properties and results of the preparation of polymeric fluorophores. The fluorophores were characterized through the data from proton NMR, IR and elemental analysis. IR spectra of the synthesized polymer showed the new ester carbonyl stretching and urethane carbonyl bands at 1740 and 1715 cm^{-1}, respectively, and drastic increase in intensity of the aliphatic C–H stretching band at 2880–2940 cm^{-1}. NMR spectra of aromatic protons of perylene and anthracene ring appeared at 8.22 and 7.70 ppm, respectively and the methylene protons appeared at 1.52 ppm. The average molecular weight of the copolymers was 11136–16100 with a MWD of 2.2–2.6 by GPC. Both polymers were soluble in common organic solvents such as acetone, chloroform, tetrahydrofuran, 1,2-dimethoxyethane, *N,N*-dimethylformamide, *N*-methylpyrrolidone and dibutylphthalate. Homogeneous and pinhole-free thin films can be obtained by spin coating from cyclohexanone solution.

3.3. Optical properties of copolymers containing red and blue chromophores

The UV absorbance, photoluminescence and chemiluminescence of the polyester fluorophores were measured and listed in Table 2. The UV–vis absorption spectra of perylene tetracaboxydiimide- and diphenyl anthracene-containing monomers and copolymer fluorophores were shown in Fig. 1. The

Table 1
Properties of the monomeric and polymeric fluorophores

No.	Copolymer (**1**/**2**)	mp (°C)	η_{inh}[a]	MW[b]	MWD[c]	Yield (%)
1	–	231	–	1090	–	23
2	–	212	–	450	–	87
3	1/10	–	0.36	14 100	2.4	91
4	1/20	–	0.41	16 100	2.6	92
5	1/10	–	0.37	13 600	2.2	91
6	1/20	–	0.38	15 200	2.4	93

[a] Inherent viscosity was obtained at a concentration of 0.5 g/dl in dibutylphthalate at 25 °C.

[b] MW, molecular weight.

[c] MWD, molecular weight distribution.

Table 2
The UV–vis absorption, photoluminescence and chemiluminescence maximum wavelength of the monomeric and polymeric fluorophores

No	UV–vis[a]	PL[b] (nm)	CL[c] (nm)	Intensity[d] (cd/cm^2)		Color	
				1 min	60 min	Solid state	DBP
1	592	625	623	14.1	2.1	Brown	Red
2	400	441	453	13.2	1.93	Yellow	Blue
3	400 569	421 604	423 620	12.1	2.76	Violet	Red violet
4	396 568	436 604	439 614	14.8	1.45	Light violet	Violet
5	396 566	428 605	431 620	13.3	1.72	Violet	Red violet
6	398 567	430 605	439 616	14.9	1.52	Light violet	Violet

[a] UV–vis spectra were obtained at a concentration of 10^{-4}–10^{-5} mol/l in chloroform.

[b] Photoluminescence in chloroform.

[c] Chemiluminescence in dibutylphthalate.

[d] The intensity measured with a 0.3 wt.% of fluorophore in dibutylphthalate.

absorption intensity at the blue side ($\lambda_{\max}\sim$397 nm) and the red side ($\lambda_{\max}\sim$588 nm) of spectral region appeared to systematically change according to the content of diphenyl anthracene and pherylene tetracarboxydiimide moiety.

Photoluminescence spectra of polymers **3**–**6** are compared in Fig. 2. Upon ultraviolet excitation, solution of the polymers exhibited the very intense violet fluorescence with the two absorption maxima at 428–436 nm and 604–605 nm. The photoluminescence spectrum of **3**–**6** with maximum wavelength showing a typical blue or red color appeared at 440 nm and 625 nm, respectively. The wavelength at the maximum of the emitting light moved toward the shorter wavelength in the photoluminescence of polymers **3**–**6** compared with that of monomer. The shift of the maximum wavelength could be due to the electronic effect. The electron density of the anthracene ring becomes deficient by an electron-attracting acyloxy group in diphenyl anthracene, therefore shifted to the shorter wavelength [14].

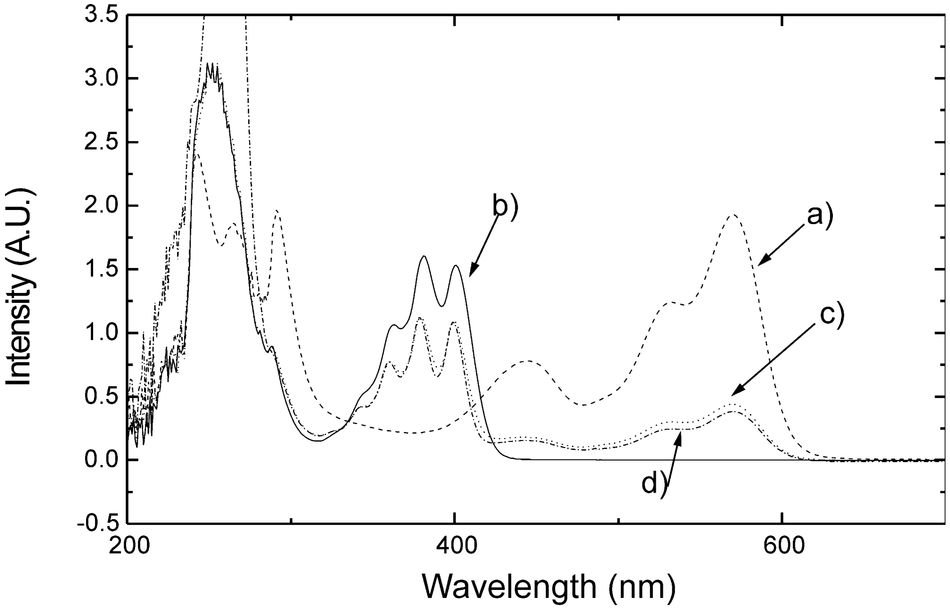


Fig. 1. The UV–vis absorption spectraof (a) **1**, (b) **2**, (c) **3** and (d) **4**.

3.4. Chemiluminescence of copolymer dyes

An aliquot of the hydrogen peroxide and sodium salicylate catalyst solution was added into the solution of fluorophore and CPPO at 25 °C. It was found that the earlier monomer **1** and **2**, and polymers **3**–**6** were highly efficient red or blue fluorophores, which are highly soluble in the dibutylphthalate system of the chemiluminescent reaction. As soon as the two components were mixed, the emission spectrum was immediately scanned. The chemiluminescence spectra were similar to

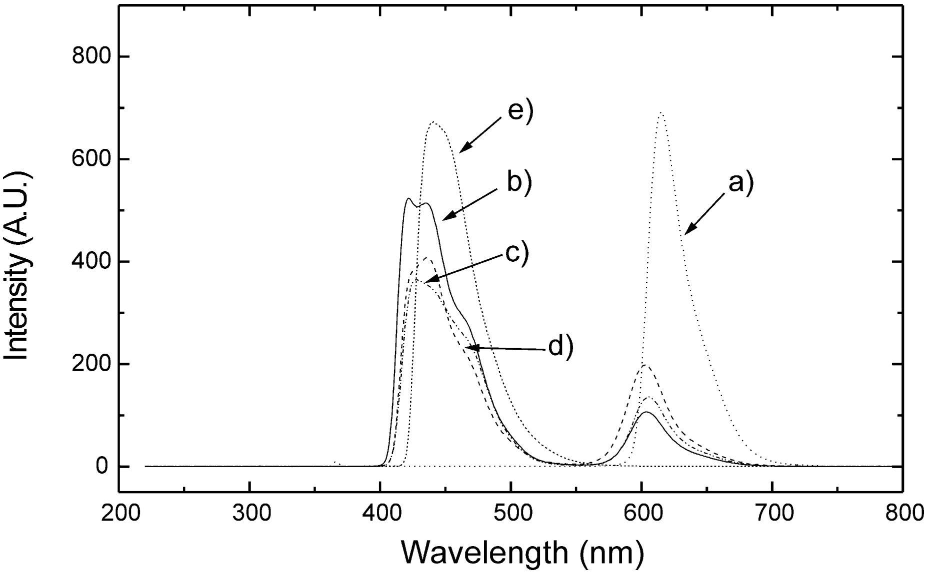


Fig. 2. Photoluminescence spectra of (a) **1**, (b) **3**, (c) **4**, (d) **5** and (e) **2**.

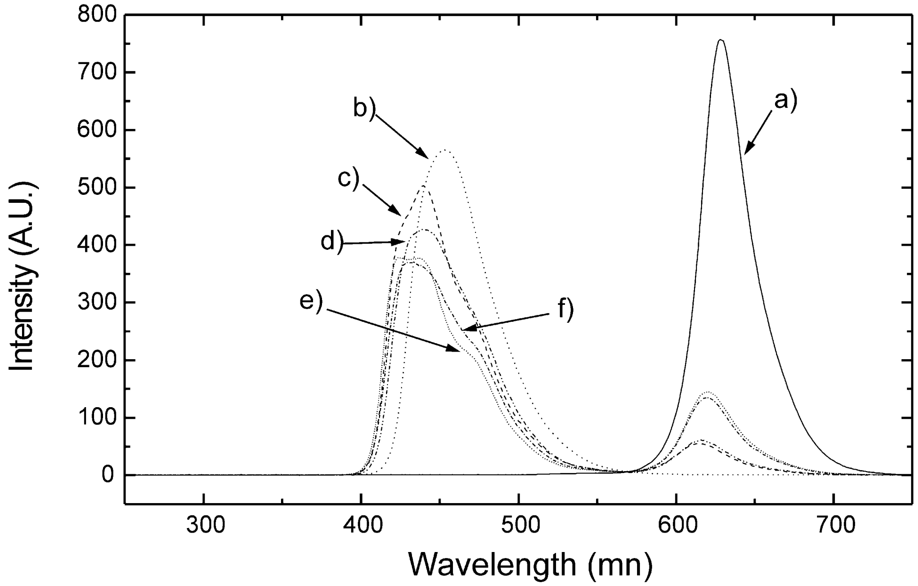


Fig. 3. Chemiluminescence spectra of (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5** and (f) **6**.

normal photoluminescence spectrum as shown in Figs. 2 and 3. Typical violet light emission has been observed from the chemiluminescence of fluorophores **3–6**. Fig. 4 showed a chemiluminescence emission light in the CIE chromaticity diagram of fluorophores **1–6**. Generally, the color of fluorophore is dependent on the conjugation length of the fluorophore and substituents as auxochromophore [15]. The substituents such as alkyl, alkoxy and halogen group made the fluorophores emit light at longer wavelength in the visible region. Phenoxy-substituted perylene tetracaboxydiimide or diphenyl anthracene polymers were moderate red or blue light emitting fluorophores.

Chemiluminescence arises whenever a chemical reaction produces an electronically excited product that either emits direct light while returning to the ground state or transfers its energy to another molecule, a fluorophore, which emits the light. This group of molecules was based on oxidation of an oxalate ester by hydrogen peroxide [1,2]. It is required that the fluorescence dye should be stable in the presence of hydrogen peroxide. The highly conjugated fluorophore systems were not often

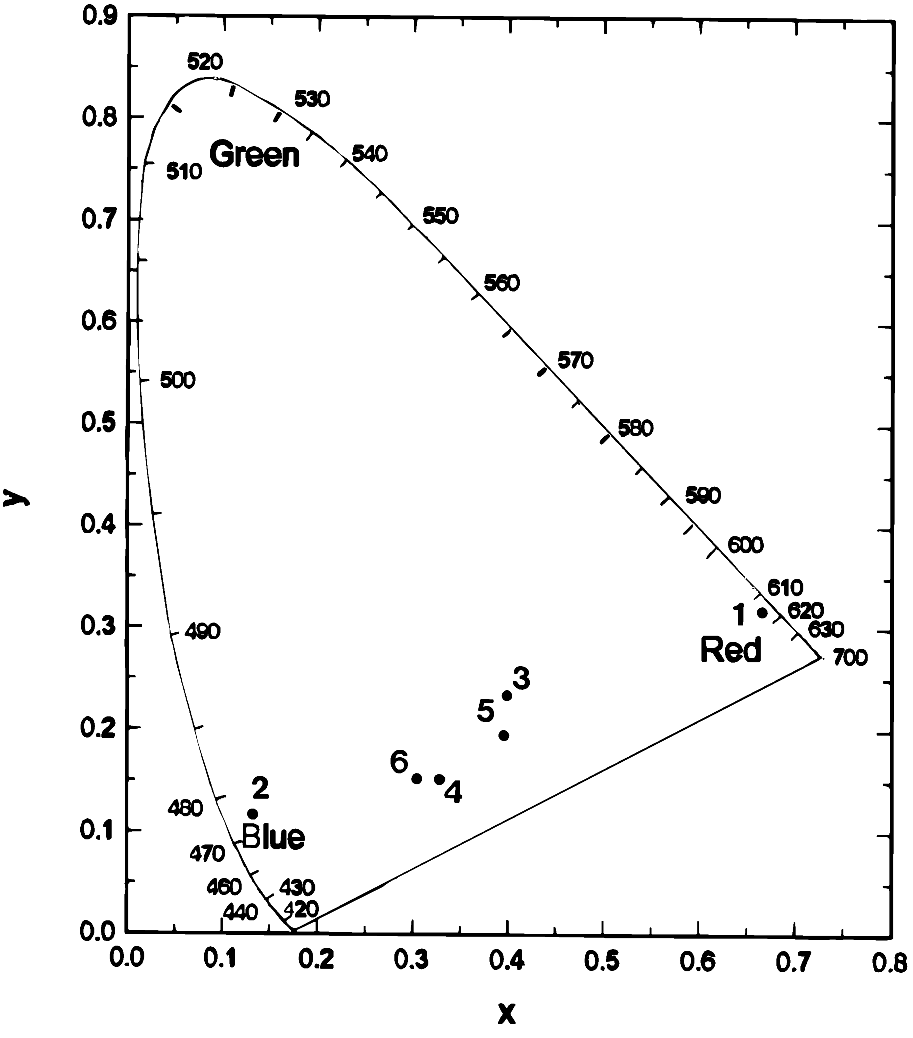


Fig. 4. CIE chromaticities diagram of monomer and polymeric fluorophores **1–6**.

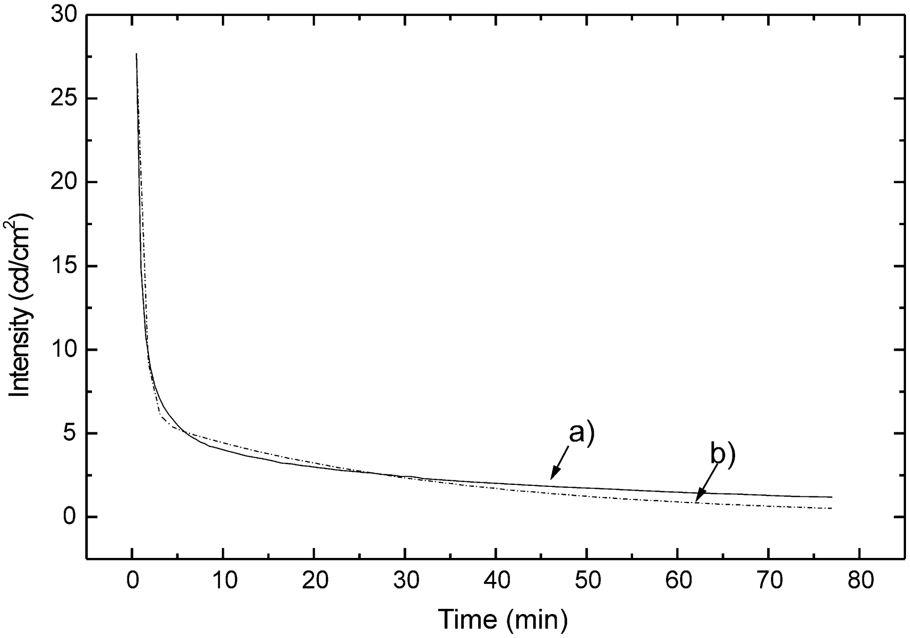


Fig. 5. Biexponential chemiluminescence decay curve for (a) polymeric fluorophore **6** and dibutylphthalate at room temperature, (b) biexponential expression $I = 43.459e^{-1.416t} + 6.109e^{-0.032t}$.

resistant to oxidation in the presence of peroxide. The perylene tetracarboxylicdiimide moiety was quite resistant to peroxide oxidation. It was already reported that the CIE coordination value $x = 0.6939$, $y = 0.3053$ for polymeric fluorophore containing **1** unit changed to $x = 0.6664$, $y = 0.3022$ during chemiluminescent reaction [10]. As the chemiluminescence reaction proceeded, the CIE coordination value of copolymers emitting violet light changed a little.

The light intensity–decay time data were taken immediately after mixing the reagent and measured for 75 min. The decay intensities of the chemiluminescence for the monomeric and polymeric fluorophores were shown in the Fig. 5. When the intensity of polymeric fluorophores was compared with **1** and **2**, polymeric fluorophores **3–6** normally emit in the violet light region with good efficiency as indicated in Table 2. As the figure shows the light intensity decayed to approximately 50% of the maximum value at a few minute. But the chemiluminescence emission maintained for longer than 24 hr and was visible with the naked eye. The polymeric fluorophores showed similar light intensity to the monomeric compound in Table 2.

These decay profiles can be fitted to following biexponential rate curves.

$$I = 43.459e^{-1.416t} + 6.109e^{-0.032t}$$

The maximum brightness of chemiluminescence was ca.12–15 cd/m^2 just after mixing the sample and decreased to 1–3 cd/m^2 after 1 h, respectively.

4. Conclusion

Diphenyl anthracene- and perylene tetracarboxydiimide derivatives-containing monomer and copolymers were found to be efficient fluorophores for chemiluminescence and stable under peroxide oxidative condition. The fluorophores showing a light emission with 423–439 nm and 614–620 nm were applicable to violet polymeric fluorescence dye for the chemiluminescence.

Acknowledgements

This work was supported by Korea Research Foundation Grant KRF-2001-015-DP0256.

References

[1] Chandross EA. Tetrahedron Lett 1963;19:761.

[2] McCapra F. Acc Chem Res 1976;9:20 l.

[3] Nieman T. Detection based on solution-phase chemiluminescence system. In: Birks JW, editor. Chemiluminesence and photochemical reaction detection in chromatography. New York: VCH, 1989. p. 99–123.

[4] Akio T, Masako M, Hidetoshi A. In: Knox V-D, editor. Bio and chem: instruments and applications, vol 1 (Chapter 8). Boca Raton, FL: CRC-Press Inc, 1985.

[5] Mark HF. Encyclopedia of chemical technology, vol. 5. New York: John Wiley & Sons, 1979.

[6] Iden R, Seybold G. US Patent 4667036 (1987).

[7] Lee CW, Cho JH, Gong MS. Polymer (Korea) 1998;22:714.

[8] Lee CW, Kim C, Rhee HW, Gong MS. Bull Korean Chem Soc 2000;21:701.

[9] Rhee HW, Kim C, Gong MS. Bull Korean Chem Soc 2001;22:727.

[10] Lee CW, Shim JJ, Gong MS, Synth Met (in press).

[11] Quante H, Schlichting P, Rohr U, Geerts Y, Mullen K, Macromol Chem Phys 1996; 197: 4029.

[12] Mohan AG, Turro NJ. Chem Edu 1974;51:528.

[13] Clarke HT, Taylor ER. Org Synth Collective Volumes 1932;1:150.

[14] Kraft A, Grimsdale AC, Holmes AB. Angew Chem Int Ed 1998;37:403.

[15] Zolinger H. Colour chemistry. New York: VCH, 1991.