

The Fluorescent Quantum Efficiency of Copolymers Containing Coumarin-6 at the Side-chain

Jung-An Cheng, Chang-Ping Chang, Chin-Hsin Chen and Mu-Shih Lin*

Department of Applied Chemistry, National Chiao-Tung University, Hsinchu 30050, Taiwan

(*Author for correspondence; E-mail: mlin43@seed.net.tw)

Key words: concentration quenching, coumarin-6, excimer, fluorescent quantum efficiency, photoluminescence

Abstract

Coumarin-6 containing acrylates (CA) with different spacers were synthesized. Copolymers of CA with methyl methacrylate (MMA) in CA/MMA in the weight ratios of 1/20, 1/40 and 1/60 were prepared by using AIBN as initiator. The copolymer compositions were determined from uv-visible spectroscopic analyses, according to Beer's law. UV absorption and photoluminescence (PL) spectra indicated a concentration quenching, which increased with increasing coumarin-6 concentration in the copolymer compositions and also increasing the spacer length from the copolymer to coumarin-6 moiety, leading to a decreased fluorescence efficiency (φ_s/φ_o) as well as a red shift of λ_{\max} . Furthermore, as the spacer, n in $-(\text{CH}_2)_n-$, increases from $n = 2, 3$ to 6, excimers formed due to overlap of chromophores, resulting in the splitting of the PL emission band and lowering the PL intensity. Experimental results revealed that when the ratio of CA/MMA = 1/60 and the spacer $n = 2$, the copolymer film showed an optimized fluorescent quantum efficiency.

Introduction

The phenomenon of organic electroluminescence was first discovered by Pope in 1963 [1]. The development of an organic light-emitting device (or diode; OLED) actually began when Tang reported the first highly efficient multi-layer OLEDs [2]. One of the key developments in the advancement of OLED display technology can be attributed to the discovery of the guest-host doped emitter system [3]. Coumarin-6 (C-6), a chromophore of highly conjugated coplanar molecule, is well known as a fluorescent material, which absorbs uv at a λ_{\max} of 443 nm and PL with a peak emission maximum at 543.2 nm [4, 5]. Coumarin-6 is also available in a multilayer OLED by thermal deposition [6, 7]. For ease of processing, organic dyes of high quantum efficiency were blended with the spin-coatable polymeric matrix or, simply using the synthetic approaches to place the chromophore onto the polymeric backbone as a pendant group, to afford a solution processible OLED [8, 9]. Dendrimer-type materials were also described in the literature [10]. A typical application of coumarin-6 in multilayer OLED emission layers, where the electrons recombine with the holes, releases energy in the form of a green light [6]. However, if the chromophore concentration is above a critical level, concentration quenching would occur and cause a decreased PL intensity, which subsequently leads to a lower fluorescent quantum efficiency [11]. In this work, we developed a solution processible OLED based on copolymers containing coumarin-6 as a pendant group with different spacers. By a synthetic approach, coumarin-6 was appended onto the poly(methyl methacrylate) backbone, with spacers

of 2, 3 and 6 methylene units. We found that the spacer length played an important role in the PL emission and also affected the quantum efficiency. In order to reach a maximum fluorescent quantum efficiency for a possible application in polymer light emitting diode (PLED), we tried to optimize the coumarin-6 level and spacer length in the copolymers to suppress the concentration quenching effects.

Experimental

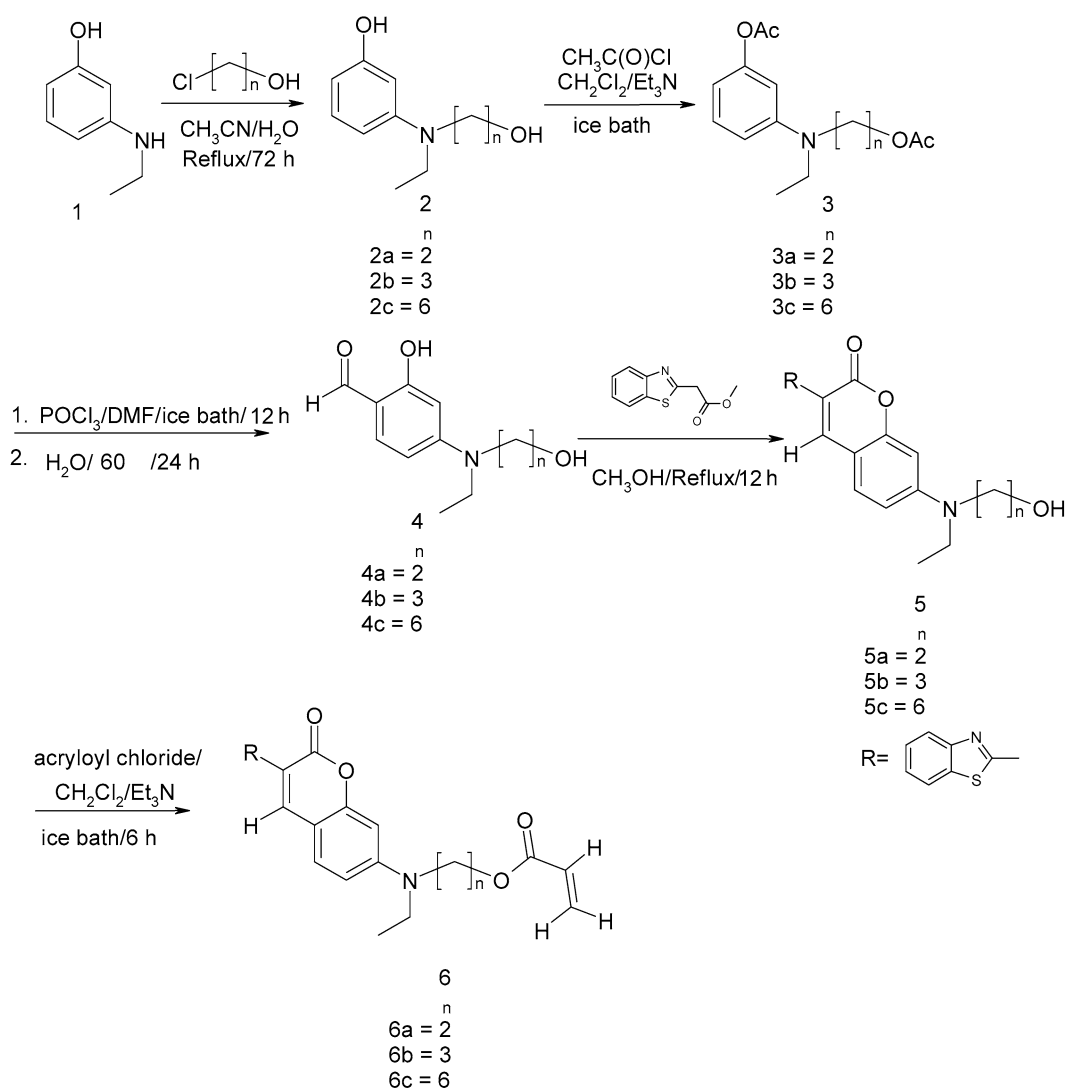
Instrumentation

^1H NMR (Bruker AM-300) and FTIR (Nicolet 520) were used to verify the structures of synthesized compounds and copolymers. DSC data were recorded with a Seiko SSC 5200 DSC under nitrogen atmosphere with a heating rate of 10 °C/min. UV-visible spectra were obtained with a Beckman DU 520 Spectrometer. Copolymer composition analyses were done based on calibration of monomer concentration according to Beer's law. Copolymer films were spin-coated from solution on well cleaned ITO glass by a SYNREX SSP-01A coater, with a film thickness ranging from 500 to 800 Ångstroms. PL spectra of the film samples were recorded with a Shimadzu RF-5310PC spectrofluorophotometer. The PL peak areas were integrated for the calculation of fluorescent quantum efficiency.

Materials

All compounds and copolymers were prepared according to the synthetic scheme.

Synthetic Scheme of chromophores



Preparation of Compound 2

In a 250 ml three-neck flask equipped with a magnetic stirrer and a condenser were placed 3-ethylaminophenol (**1**) (1.00 g, 7.30 mmole), CaCO₃ (2.92 g, 29.20 mmole), chloroalkanol (9.49 mmole), D.I. water (10 ml), and CH₃CN (10 ml). The mixture was refluxed for 72 h. After cooling, the mixture was filtrated and extracted with ethyl acetate, dried with anhydrous MgSO₄, and then concentrated. The crude product was purified by passing through silica gel with eluent (EA/hexane = 1 : 1) to afford a light brown oil **2**. The yield of 3-(ethyl-2-hydroxyethylamino)phenol (**2a**) was 1.12 g (85.0%). *R_f*(EA/hexane = 1 : 1) = 0.37. ¹H NMR (CDCl₃, 300 MHz) 1.134 (t, 3H), 3.383 (m, 4H), 3.768 (t, 2H), 6.147 (dd, *J* = 8.1 Hz, 1H), 6.228 (s, 1H), 6.325 (dd, *J* = 8.1 Hz, 1H), 7.043 (t, 1H). IR (KBr) 3343.46, 1615.86, 1210.86 cm⁻¹. EI-Mass (*m/z*; rel. intensity %) 182 (M⁺+1, 3.56), 181 (M⁺, 32.64), 150 (100). The yield of 3-(ethyl-3-hydroxypropylamino)phenol (**2b**) was 1.00 g (70.3%). *R_f*(EA/hexane = 1 : 1) = 0.33. ¹H NMR

(CDCl₃, 300 MHz) 1.110 (t, 3H), 1.815 (m, 2H), 3.325 (m, 4H), 3.723 (t, 2H), 6.148 (dd, *J* = 8.7 Hz, 1H), 6.219 (s, 1H), 6.288 (dd, *J* = 10.2 Hz, 1H), 7.007 (t, 1H). IR (KBr): 3311.17, 2967.44, 2882.60, 1615.88, 1577.20, 1209.70, 1166.54 cm⁻¹. EI-Mass (*m/z*; rel. intensity %): 196 (M⁺+1, 4.09), 195 (M⁺, 36.36), 150 (100). The yield of 3-(ethyl-6-hydroxyhexylamino)phenol (**2c**) was 1.36 g (78.7%). *R_f*(EA/hexane = 1 : 1) = 0.38. ¹H NMR (CDCl₃, 300 MHz): 1.125 (t, 3H), 1.320 (m, 2H), 1.564 (m, 2H), 3.224 (t, 2H), 3.325 (m, 2H), 3.664 (t, 2H), 6.142 (dd, *J* = 8.1 Hz, 1H), 6.200 (s, 1H), 6.242 (dd, *J* = 8.7 Hz, 1H), 7.042 (t, 1H). IR (KBr): 3332.55, 2933.72, 2854.31, 1613.41, 1210.60 cm⁻¹. EI-Mass (*m/z*; rel. intensity %): 237 (M⁺, 16.53), 150 (100).

Preparation of Compound 3

In a 250 ml three-neck flask equipped with a magnetic stirrer and a condenser were placed compound **2** (5.52 mmole), triethylamine (0.67 g, 6.63 ml) and dichloromethane (20 ml).

Under a nitrogen atmosphere, the mixture was stirred for 15 min in an ice bath. Acetic chloride (0.52 g, 6.62 m mole) in dichloromethane (5 ml) was added by syringe. The mixture was kept stirring for 6 h. The reactant was decanted into ice water and extracted with ethylacetate. The organic layer was collected, dried with anhydrous MgSO_4 , and concentrated with a rotary evaporator. The crude product was purified by passing through silica gel with eluent (EA/hexane = 1 : 1) to afford a light yellow oil **3**. The yield of **3a** was 1.41 g (96.0%). R_f (EA/hexane = 1 : 1) = 0.79. $^1\text{H NMR}$ (CDCl_3 , 300 MHz): 1.162 (t, 3H), 2.043 (s, 3H), 2.281 (s, 3H), 3.391 (q, 2H), 3.526 (t, 2H), 6.381 (s, 1H), 6.406 (s, 1H), 6.578 (dd, $J = 8.1$ Hz, 1H), 7.185 (t, 1H). IR (KBr): 2910.30, 1764.74, 1739.43, 1611.24, 1500.20, 1213.01 cm^{-1} . EI-Mass (m/z; rel. intensity): 265 (M^+ , 20.63), 205 (4.07), 193 (10.42), 192 (100), 150 (37.10), 122 (4.37). The yield of **3b** was 1.45 g (94.0%). R_f (EA/hexane = 1 : 1) = 0.80. $^1\text{H NMR}$ (CDCl_3 , 300 MHz): 1.143 (t, 3H), 1.910 (m, 2H), 2.077 (s, 3H), 2.265 (s, 3H), 3.343 (m, 4H), 4.118 (t, 2H), 6.335 (m, 2H), 6.548 (dd, $J = 8.3$ Hz, 1H), 7.174 (t, 1H). IR (KBr): 2965.75, 2925.97, 1765.75, 1739.23, 1613.26, 1208.84 cm^{-1} . EI-Mass (m/z; rel. intensity %): 279 (M^+ , 14.41), 193 (10.88), 192 (100), 178 (5.04), 151 (3.20), 150 (35.59), 122 (4.15), 101 (3.90). The yield of **3c** was 1.60 g (90.2%). R_f (EA/hexane = 1 : 1) = 0.83. $^1\text{H NMR}$ (CDCl_3 , 300 MHz): 1.122 (t, 3H), 1.361 (m, 2H), 1.614 (m, 2H), 2.032 (s, 3H), 2.267 (s, 3H), 3.211 (t, 2H), 3.237 (m, 2H), 4.050 (t, 2H), 6.284 (s, 1H), 6.475 (dd, $J = 8.4$ Hz, 1H), 6.475 (dd, $J = 8.4$ Hz, 1H), 7.151 (t, 1H). IR (KBr): 2933.14, 2859.56, 1766.42, 1736.44, 1612.74, 1212.56 cm^{-1} . EI-Mass (m/z; rel. intensity %): 321 (M^+ , 9.19), 193 (9.19), 192 (100), 150 (21.16), 122 (6.16).

Preparation of Compound 4

In a 250 ml three-neck flask equipped with a magnetic stirrer and a condenser was placed dried DMF (2.75, 37.67 m mole) in an ice bath. POCl_3 (0.67 g, 6.63 ml) was added dropwise and stirred under nitrogen for 40 min. Compound **3** (18.87 m mole) in DMF (5.0 ml) was added and kept stirring in an ice bath for 20 min. The ice bath was removed and the reaction mixture was stirred for an additional 12 h at room temperature. Ice water (10 ml) was added and stirred at 60 °C for another 24 h. The mixture was decanted in ice water (50 ml), and extracted with ethylacetate. The organic layer was collected, dried with anhydrous MgSO_4 , and concentrated by rotary evaporator to obtain a brown oil of compound **4**. The crude compound **4** was used for the next reactions without further purification. Yields of **4a**, **4b** and **4c** are 95.70%, 89.00% and 85.45%, respectively.

Preparation of Compound 5

A 250-ml three-neck flask equipped with a magnetic stirrer and a condenser were placed **4** (4.78 m mole), methanol (10 ml), ethylbenzothiazole-2-acetate [12] (1.06 g, 4.80 m mole) and drops of piperidine. The mixture was then refluxed under a nitrogen atmosphere for 12 h. The reactant was filtered. The filtrate was collected, washed with methanol/water (MeOH = 90 vol%), and recrystallized in

methanol to afford a yellow solid **5**. The yield of 3-(2-benzothiazolyl)-7-(2-hydroethylethylamino)coumarin (**5a**) was 1.26 g (72.0%). Mp = 236–237 °C. R_f (EA/hexane = 1 : 1) = 0.31. $^1\text{H NMR}$ (CDCl_3 , 300 MHz): 1.205 (t, 3H), 3.491 (q, 2H), 3.587 (t, 2H), 3.865 (t, 2H), 6.068 (s, 1H), 6.709 (dd, $J = 11.1$ Hz, 1H), 7.331 (t, 1H), 7.455 (dd, $J = 8.7$ Hz, 2H), 7.917 (dd, $J = 7.8$ Hz, 1H), 8.020 (dd, $J = 8.7$ Hz, 1H), 8.884 (s, 1H). IR (KBr): 3327, 1707.73, 1617.27, 1593.54 cm^{-1} . EI-Mass (m/z; rel. intensity %): 367 ($\text{M}^+ + 1$, 20.63), 366 (M^+ , 31.18), 337 (8.40), 336 (22.04), 335 (100), 308 (3.46), 307 (15.32), 306 (12.90), 279 (5.65), 278 (8.33), 277 (3.24), 251 (3.04), 250 (3.26), 223 (3.88), 222 (4.37), 168 (13.71), 149 (3.33), 140 (4.44), 104 (3.13). The yield of 3-(2-benzothiazolyl)-7-(2-hydropropylethylamino) coumarin (**5b**) was 1.47 g (81.0%). Mp = 227–228 °C. R_f (EA/hexane = 1 : 1) = 0.18. $^1\text{H NMR}$ (CDCl_3 , 300 MHz): 1.231 (t, 3H), 1.888 (m, 2H), 3.565–3.451 (m, 4H), 3.745 (t, 2H), 6.592 (s, 1H), 6.710 (dd, $J = 11.4$ Hz, 1H), 7.346 (t, 1H), 7.471 (m, 2H), 7.929 (dd, $J = 7.8$ Hz, 1H), 8.003 (dd, $J = 8.4$ Hz, 1H), 8.897 (s, 1H). IR (KBr): 3444.44, 1707.62, 1612.96, 1584.68, 1199.90 cm^{-1} . EI-Mass (m/z; rel. intensity %): 381 ($\text{M}^+ + 1$, 13.14), 380 (M^+ , 67.31), 337 (6.01), 336 (18.27), 335 (100), 322 (7.05), 321 (6.57), 307 (15.71), 306 (15.30), 278 (11.78), 168 (8.73). The yield of 3-(2-benzothiazolyl)-7-(2-hydrohexylethylamino) coumarin (**5c**) was 1.71 g (85.0%). Mp = 144–145 °C. R_f (EA/hexane = 1 : 1) = 0.33. $^1\text{H NMR}$ (CDCl_3 , 300 MHz): 1.237 (t, 3H), 1.369 (m, 4H), 1.532–1.678 (m, 4H), 3.351 (t, 2H), 3.453 (q, 2H), 3.657 (q, 2H), 6.533 (s, 1H), 6.637 (dd, 1H, $J = 6.637$ Hz), 7.244 (t, 1H), 7.470 (t, 2H), 7.926 (dd, $J = 8.4$ Hz, 1H), 8.002 (dd, $J = 7.8$ Hz, 1H), 8.834 (s, 1H). IR (KBr): 3348.32, 2975.18, 2922.63, 1714.32, 1615.73, 1196.60 cm^{-1} . EI-Mass (m/z; rel. intensity %): 423 ($\text{M}^+ + 1$, 9.13), 422 (M^+ , 34.13), 337 (7.72), 336 (21.49), 335 (100), 307 (16.99), 306 (13.62), 279 (6.14), 278 (9.13), 168 (8.67).

Preparation of Compound 6

A 250 ml three-neck flask equipped with a magnetic stirrer and condenser were placed **5** (1.37 m mole), dichloromethane, and triethylamine (0.17 g, 1.68 m mole). The reactor was placed in an ice bath and stirred for 15 min. Acryloyl chloride (0.15 g, 1.66 m mole) in dichloromethane (10 ml) was added by syringe, and kept stirring for 12 h. The mixture was decanted into ice water (30 ml), and extracted with ethyl acetate. The organic layer was collected, dried with anhydrous MgSO_4 , filtrated, and concentrated by rotary evaporator. A yellow solid of compound **6** was obtained. The yield of 3-(2-benzothiazolyl)-7-(N' -2-acryloylethyl- N' -ethylamino)coumarin (**6a**) was 0.44 g (75.9%). Mp = 177–178 °C. R_f (EA/hexane = 1 : 1) = 0.67. $^1\text{H NMR}$ (CDCl_3 , 300 MHz): 1.237 (t, 3H), 3.504 (q, 2H), 3.707 (t, 2H), 4.363 (t, 2H), 5.855 (dd, $J = 11.7$ Hz, 1H), 6.099 (q, 1H), 6.405 (dd, $J = 18.6$ Hz, 1H), 6.644 (s, 1H), 6.746 (dd, $J = 11.4$ Hz, 1H), 7.356 (t, 1H), 7.474 (t, 2H), 7.935 (dd, $J = 7.5$ Hz, 1H), 8.008 (dd, 10.5 Hz, 1H), 8.914 (s, 1H). IR (KBr): 2964.67, 2922.63, 1734.89, 1707.20, 1614.38, 1590.43, 1191.43 cm^{-1} . EI-Mass (m/z; rel. inten-

sity %): 422 ($M^+ + 2$, 3.17), 421 ($M^+ + 1$, 9.76), 420 (M^+ , 32.5), 335 (100). The yield of 3-(2-benzothiazolyl)-7-(N' -3-acryloylpropyl- N' -ethylamino)coumarin (**6b**) was 0.43 g (72%). $M_p = 111\text{--}112^\circ\text{C}$. $R_f(\text{EA}/\text{hexane} = 1:2) = 0.68$. $^1\text{H NMR}$ (CDCl_3 , 300 MHz): 1.382 (t, 3H), 2.020 (m, 2H), 3.463 (m, 4H), 4.231 (t, 2H), 5.894 (dd, $J = 11.7$ Hz, 1H), 6.161 (q, 1H), 6.450 (dd, $J = 18.6$ Hz, 1H), 6.553 (s, 1H), 6.648 (dd, $J = 11.7$ Hz, 1H), 7.365 (t, 1H), 7.466 (t, 2H), 7.921 (dd, $J = 7.8$ Hz, 1H), 7.998 (dd, $J = 8.0$ Hz, 1H), 8.881 (s, 1H). IR (KBr): 2969.93, 2922.63, 1724.38, 1707.87, 1613.32, 1585.58, 1191.95 cm^{-1} . EI-Mass (m/z ; rel. intensity %): 436 ($M^+ + 2$, 4.88), 435 ($M^+ + 1$, 13.19), 434 (M^+ , 45.73), 337 (7.62), 336 (21.34), 335 (100), 322 (3.09), 321 (4.82), 307 (12.12), 306 (11.51), 279 (3.72), 278 (6.33), 140 (3.35), 113 (5.87), 55 (3.39). The yield of 3-(2-benzothiazolyl)-7-(N' -6-acryloylhexyl- N' -ethylamino)coumarin (**6c**) was 0.54 g (82.2%). $M_p = 88.5\text{--}89.5^\circ\text{C}$. $R_f(\text{EA}/\text{hexane} = 1:1) = 0.85$. $^1\text{H NMR}$ (CDCl_3 , 300 MHz): 1.262 (t, 3H), 1.429 (m, 4H), 1.571–1.766 (m, 4H), 3.373 (t, 2H), 3.476 (q, 2H), 4.181 (t, 2H), 5.838 (dd, $J = 12.3$ Hz, 1H), 6.133 (q, 1H), 6.419 (dd, 1H, $J = 18.9$ Hz), 6.556 (s, 1H), 6.660 (dd, $J = 11.1$ Hz, 1H), 7.372 (t, 1H), 7.504 (t, 2H), 7.955 (dd, 1H, $J = 7.8$ Hz), 8.027 (dd, $J = 8.4$ Hz, 1H). IR (KBr): 2965.11, 2911.17, 1730.14, 1707.24, 1613.14, 1202.64 cm^{-1} . EI-Mass (m/z ; rel. intensity %): 478 ($M^+ + 2$, 3.92), 477 ($M^+ + 1$, 9.64), 476 (M^+ , 31.25), 337 (10.68), 336 (21.61), 335 (100), 321 (4.43), 308 (3.03), 307 (13.61), 306 (11.20), 279 (3.84), 278 (5.73), 168 (5.86), 154 (3.32), 140 (3.08), 55 (3.39).

Preparation of Copolymer

In a 150 ml three-neck flask equipped with a magnetic stirrer and a condenser were placed compound **6**, methyl methacrylate, AIBN (2 wt%), and DMF (40 ml). The mixture was heated to 60°C under inert gas for 24 h. The reactants were poured into methanol (250 ml) with stirring. The copolymer was filtered and purified by dissolving in acetone (25 ml), filtered and coagulated from acetone. This purification was repeated 3 times. After drying in a vacuum oven, the following yellow solid copolymers were obtained:

P2-A Feed ratio of 6a/MMA is 0.60 g (1.43 mmole)/2.8571 g (28.57 mmole). Yield 3.04 g (88.0%). $\eta_{\text{inh}}(\text{CH}_2\text{Cl}_2; 25^\circ\text{C}) = 0.3616$ dl/g. $M_w = 84082.3$ g/mole. $M_n = 33778.3$ g/mole. T_g and T_d are 117.0°C and 304.0°C .

P2-B Feed ratio of 6a/MMA is 0.20 g (0.48 mmole)/1.9048 g (19.05 mmole). Yield 1.41 g (66.81%). $\eta_{\text{inh}}(\text{CH}_2\text{Cl}_2; 25^\circ\text{C}) = 0.2543$ dl/g. $M_w = 51329.9$ g/mole. $M_n = 31356.9$ g/mole. T_g and T_d are 111.6°C and 287.7°C .

P2-C Feed ratio of 6a/MMA is 0.13 g (0.31 mmole)/1.8571 g (18.57 mmole). Yield 1.66 g (83.75%). $\eta_{\text{inh}}(\text{CH}_2\text{Cl}_2; 25^\circ\text{C}) = 0.2718$ dl/g. $M_w = 55,463.3$ g/mole. $M_n = 34446.0$ g/mole. T_g and T_d are 109.4°C and 303.5°C .

Copolymer P3

P3-A Feed ratio of 6b/MMA is 0.40 g (0.92 mmole)/1.8433 g (18.43 mmole). Yield 1.68 g (75.1%). $\eta_{\text{inh}}(\text{CH}_2\text{Cl}_2; 25^\circ\text{C}) = 0.1734$ dl/g. $M_w = 33770.5$ g/mole. $M_n = 20771.5$ g/mole. T_g and T_d are 109.4°C and 286.0°C .

P3-B Feed ratio of 6b/MMA is 0.20 g (0.46 mmole)/1.8433 g (18.43 mmole). Yield 1.40 g (68.5%). $\eta_{\text{inh}}(\text{CH}_2\text{Cl}_2; 25^\circ\text{C}) = 0.2149$ dl/g. $M_w = 47336.5$ g/mole. $M_n = 32655.1$ g/mole. T_g and T_d are 105.6°C and 270.0°C .

P3-C Feed ratio of 6b/MMA is 0.10 g (0.23 mmole)/1.500 g (15.00 mmole). Yield 1.18 g (74.0%). $\eta_{\text{inh}}(\text{CH}_2\text{Cl}_2; 25^\circ\text{C}) = 0.2997$ dl/g. $M_w = 81942.0$ g/mole. $M_n = 52512.7$ g/mole. T_g and T_d are 107.6°C and 236.7°C .

Copolymer P6

P6-A Feed ratio of 6c/MMA is 0.50 g (1.05 mmole)/2.10 g (21.00 mmole). Yield 1.43 g (55.0%). $\eta_{\text{inh}}(\text{CH}_2\text{Cl}_2; 25^\circ\text{C}) = 0.3020$ dl/g. $M_w = 68534.0$ g/mole. $M_n = 46155.5$ g/mole. T_g and T_d are 110.4°C and 284.0°C .

P6-B Feed ratio of 6c/MMA is 0.30 g (0.63 mmole)/2.52 g (25.20 mmole). Yield 1.91 g (67.78%). $\eta_{\text{inh}}(\text{CH}_2\text{Cl}_2; 25^\circ\text{C}) = 0.3624$ dl/g. $M_w = 81469.8$ g/mole. $M_n = 49454.7$ g/mole. T_g and T_d are 108.8°C and 291.3°C .

P6-C Feed ratio of 6c/MMA is 0.20 g (0.42 mmole)/2.521 g (25.21 mmole). Yield 1.68 g (80.34%). $\eta_{\text{inh}}(\text{CH}_2\text{Cl}_2; 25^\circ\text{C}) = 0.3832$ dl/g. $M_w = 91416.7$ g/mole. $M_n = 57915.3$ g/mole. T_g and T_d are 108.8°C and 288.0°C .

Preparation of 3-(2-benzothiazolyl)-7-(diethylamino) coumarin (Coumarin 6)

In a three-neck flask equipped with a magnetic stirrer and a condenser, were placed 4-(diethylamino)salicylaldehyde (15.00 g, 77.72 mmole), ethylbenzothiazole-2-acetate (20.33 g, 91.99 mmole), and methanol (100 ml). The mixture was refluxed for 6 h then cooled. The solution was filtrated and washed with methanol (80 vol%). The crude compound was recrystallized from 1,2-dichloromethane to afford an orange solid in a yield of 23.94 g (87.76%). $M_p = 215\text{--}216^\circ\text{C}$. $R_f(\text{EA}/\text{Hexane} = 1:1) = 0.78$. $^1\text{H NMR}$ (CDCl_3 , 300 MHz): 1.299 (t, 6H), 3.475 (q, 4H), 6.577 (s, 1H), 6.678 (dd, $J = 11$ Hz, 1H), 7.372 (t, 1H), 7.476 (m, 2H), 7.731 (dd, $J = 7.8$ Hz, 1H), 8.028 (dd, $J = 7.8$ Hz, 1H), 8.920 (s, 1H). IR (KBr): 3054.01, 2975.18, 1711.55, 1614.04, 1191.39 cm^{-1} . EI-Mass (m/z ; rel. intensity %): 352 ($M^+ + 2$, 6.34), 351 ($M^+ + 1$, 18.78), 350 (M^+ , 78.11), 337 (7.84), 336 (22.26), 335 (100), 307 (15.55), 306 (14.80), 279 (5.60), 278 (10.32), 222 (5.04), 175 (6.84), 168 (16.29).

Results and Discussions

Acrylates (CA) containing coumarin-6 of the structures **6a**, **6b** and **6c** with different spacers of 2, 3 and 6 methylene units were synthesized according to the synthetic

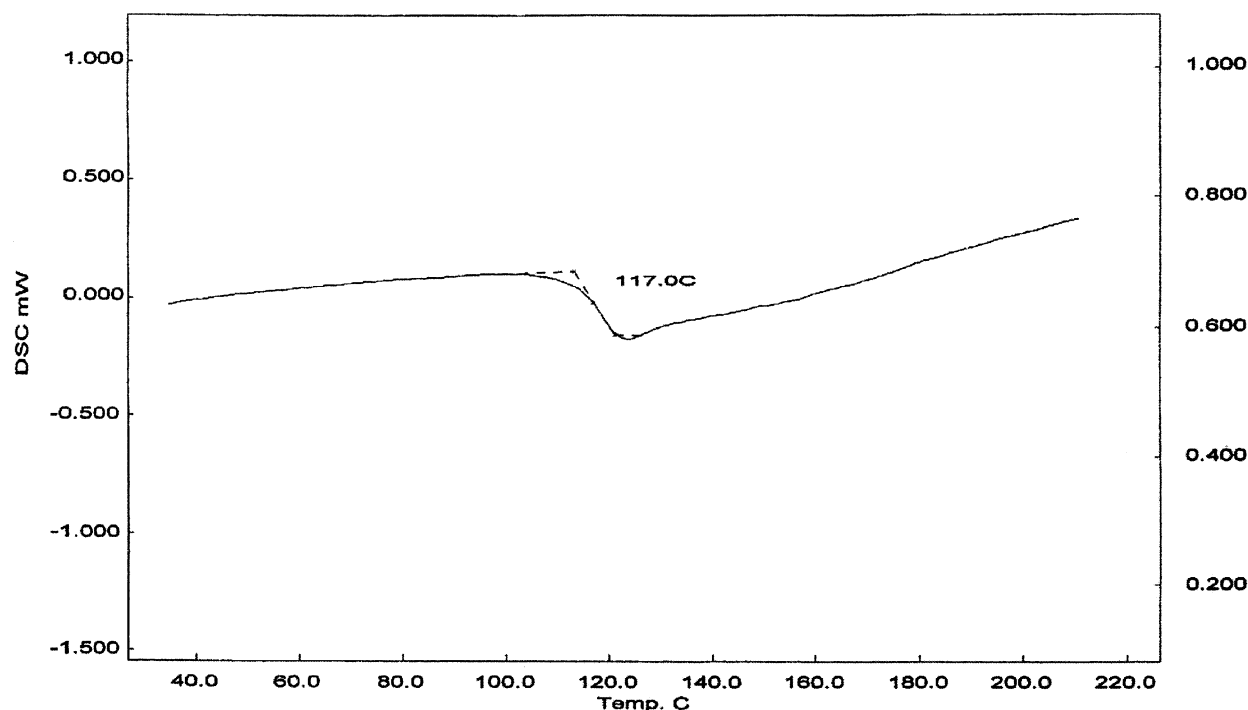


Figure 1. DSC thermogram of a typical C-6/MMA copolymer.

Table 1. The effect of chromophore concentration and spacer length on the uv-visible and PL absorptions for various solid copolymer films

Copolymer	FWHM (nm)		λ (nm)		Film thickness (Å)	Copolymer composition cpd 6/MMA molar ratio	Intensity at $\lambda_{\max, PL}$
	PL	UV-Vis	PL	UV-Vis			
P2-A	115.2	72.5	556.4	441.0	602	0.0358	2.620
P2-B	96.7	69.8	499.8	443.0	715	0.0133	2.770
P2-C	84.0	65.8	499.5	443.8	489	0.0118	3.091
P3-A	109.5	73.0	534.0	443.5	538	0.0355	1.989
P3-B	92.8	87.0	504.5	443.0	736	0.0168	2.526
P3-C	64.5	67.2	496.5	443.5	530	0.0155	3.436
P6-A	120.4	80.1	559.6	447.0	700	0.0202	1.600
P6-B	114.5	44.3	503.6	448.0	529	0.0156	2.268
P6-C	110.5	59.7	501.8	447.0	780	0.0124	1.620

scheme. Copolymers containing various ratios of **6a**/MMA, **6b**/MMA and **6c**/MMA were obtained by free radical copolymerization. Structures of all compounds and copolymers were verified with ^1H NMR and FTIR as mentioned in the experimental section. Copolymer compositions were analyzed from uv-visible data according to Beer's law. Calculated reactivity ratios are: r_1 (**6a**) = 1201, r_2 (MMA) = 118 with $r_1/r_2 = 10.2$ for P2; r_1 (**6b**) = 682, r_2 (MMA) = 78 with $r_1/r_2 = 8.74$ for P3; r_1 (**6c**) = 267, r_2 (MMA) = 80 with $r_1/r_2 = 3.34$ for P6. It appears that increasing the flexible spacer length decreases the reactivity of coumarin-6 moiety, presumably because the random coil of the flexible chain hindered the attacking radical during copolymerization. All copolymer films were spin-coated from solution. Figure 1 shows a typical DSC thermogram for a copolymer. Glass transition temperatures (T_g 's) for this series of copolymers are in the range of 105 °C to 117 °C.

Results of uv-visible and PL spectra for various CA/MMA copolymers in various spacer lengths of n in

$n = 2, 4$ and 6 are presented in Table 1. A typical figure of uv-visible spectrum is given; for example, Figure 2 shows the uv-visible spectrum for solid film of copolymers **P2**'s; whereas their corresponding PL spectra are given in Figure 3. Here, the coumarin-6 moiety level in the copolymers is in the order: A (CA/MMA = 1/20) > B (CA/MMA = 1/40) > C (CA/MMA = 1/60). The spacer, alkyl chain length, $-(\text{CH}_2)_n-$, increases from $n = 2, 3$ to 6 and the copolymers are denoted as **P2**, **P3**, to **P6**, respectively. For the same spacer, it is noted from Table 1 that an increase in the concentration of coumarin-6 increases UV absorbance but decreases the PL intensity associated with a red shift to longer wavelength and broader FWHM (full width at the half maximum). This phenomenon is known as "concentration quenching" [11], which is due to the increasing interaction between the excited state and the ground state of coumarin-6 moieties, known as excimers. Figure 4 depicts the effect of spacer length on the PL intensity. In a short spacer (where $n = 2$ or 3) and low coumarin-6 con-

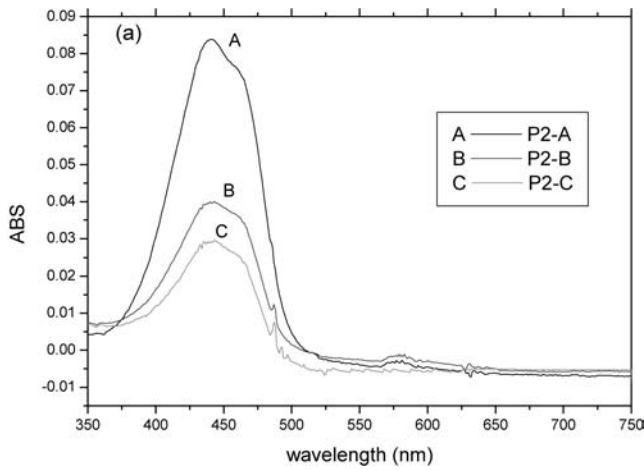


Figure 2. The uv-visible spectra of copolymer **P2**'s in solid films.

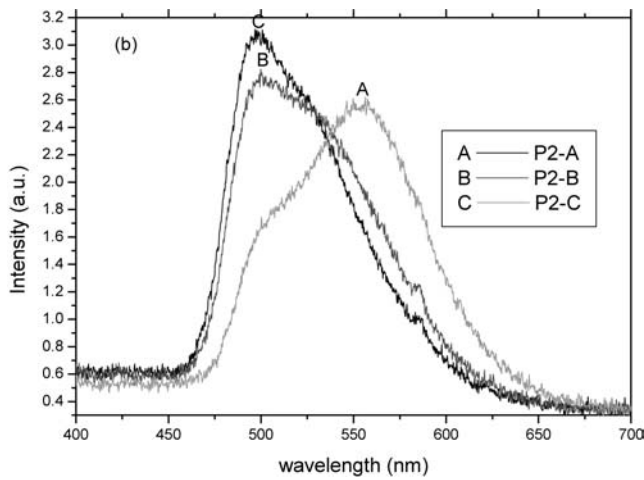


Figure 3. The PL spectra of copolymer **P2**'s in solid films.

centration, the coumarin-6 moieties are relatively far apart which induces little interaction, and no apparent concentration quenching is observed. On the contrary, in a longer spacer where $n = 6$ and higher coumarin-6 level, overlapping of coumarin-6 moieties occurs, which induces more chromophore interaction and self-absorption, leading to a pronounced quenching.

The effect of spacer length on the PL intensity and band width is obvious when comparing the data in Table 1. Under similar coumarin-6 level, excimers have lower energy level and hence shift the PL to longer wavelength (red shift) and broaden the band width [13–15]. In comparison with the effect of spacers on the photoluminescence, the splitting of peak in Figure 5 (copolymer **P6**'s) explains the existence of excimers [16]. The splitting peaks for copolymer **P6-A** occur at 500 nm and 555 nm, which shows relatively similar emission peak wavelengths for the copolymer **P2-C** of short spacer and low coumarin-6 level, as well as the copolymer **P2-A** of short spacer and high coumarin-6 level. In a longer spacer and higher chromophore concentration for copolymers **P6-A** and **P6-B**, the photoluminescence occurs at a longer and a broader peak emission wavelength, and thus accounts for the red shift [16]. This phenomenon was also found for the copolymer **P6-C** of longer spacer and low

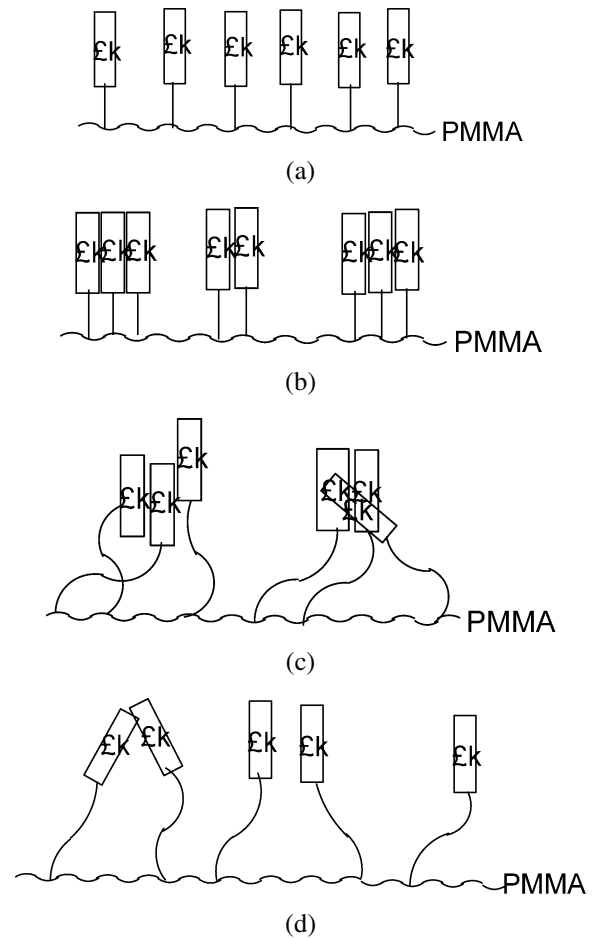


Figure 4. The effect of spacer length between PMMA backbone and chromophore on PL intensity: (a) low chromophore concentration with short spacer in copolymer; (b) high chromophore concentration with short spacer in copolymer; (c) high chromophore concentration with long spacer in copolymer; and (d) low chromophore concentration with long spacer in copolymer.

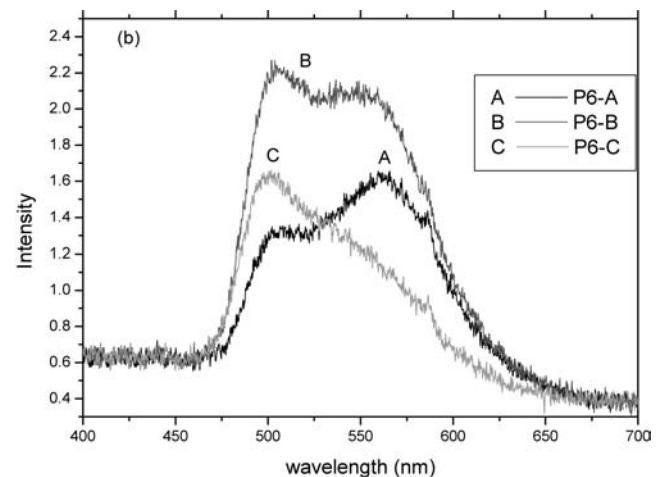


Figure 5. The PL spectra of copolymer **P6**'s in solid films.

coumarin-6 level, which showed a broad PL emission peak with a shoulder.

The fluorescent quantum efficiency is calculated according to Eq. (1) [17]:

$$\varphi_s/\varphi_o = (A_s/A_o) \times (A_{\text{ABS},O}/A_{\text{ABS},S}) \times (Q_o/Q_s), \quad (1)$$

Table 2. Data of PL and uv-visible absorptions together with the calculated quantum efficiencies for various solid copolymer films

Copolymer	λ_{\max} (nm)		Area (under PL curve)	ABS at 443.0 nm	φ_s/φ_o	cpd 6/MMA molar ratio
	PL	UV-Vis				
P2-A	557.0	441.0	223.4509	0.0500	1.24	0.0358
P2-B	502.2	446.0	282.9933	0.0463	1.69	0.0133
P2-C	498.6	442.8	334.8985	0.0467	1.98	0.0118
P3-A	525.0	443.0	112.3402	0.0487	0.638	0.0355
P3-B	501.5	443.0	112.3416	0.0523	0.996	0.0168
P3-C	496.5	443.0	318.0047	0.0422	2.08	0.0155
P6-A	501.2	448.0	252.9186	0.0573	1.22	0.0202
P6-B	504.0	447.0	237.3578	0.0612	1.07	0.0156
P6-C	503.3	445.5	224.3781	0.0432	1.44	0.0124
Coumarin 6	504.0	443.0	188.0326	0.0520	1.00	0.0150

where φ_s and φ_o are the fluorescent quantum yields of the sample and the standard (i.e., PMMA film containing 5 wt% of coumarin-6); A_s and A_o are the PL peak areas for the sample and the standard; $A_{\text{ABS},s}$ and $A_{\text{ABS},o}$ are the uv absorbances for the sample and the standard; Q_s and Q_o are the number of quanta absorbed by the sample and the standard, respectively, from the fluorescence source. In this experiment, $Q_o/Q_s = 1$ under the same fluorescence source. The calculated fluorescent quantum efficiencies for various copolymers are given in Table 2. It is generally found that increasing efficiency is observed for copolymers with a shorter spacer and lower coumarin-6 level. Thus P2-C and P3-C are the promising copolymers for further possible PLED application.

Conclusions

All copolymers prepared in this study contain the same coumarin-6 moiety, hence both coumarin-6 molecule and copolymers basically show very similar UV and PL spectra. Concentration quenching occurs at the high coumarin-6 level, leading to decreased PL intensity and red shift with broader FWHM, and this accounts for the lower fluorescent quantum efficiency. A long spacer ($n = 6$) could induce overlapping of the coumarin-6 chromophore, forming excimer which also lowers the PL intensity and causes peak splitting and red shift. Calculated data reveal that copolymers with short spacer and lower coumarin-6 level have higher fluorescent quantum efficiency.

Acknowledgement

The authors would like to express their appreciation to the National Science Council of Taiwan for financial support under contract No. 90-2216-E-009-021.

References

1. M. Pope, H. P. Kallmann and P. Magnante, *J. Chem. Phys.*, **38**, 2042 (1963).
2. C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, **51**, 913 (1987).
3. C. W. Tang, S. A. VanSlyke and C. H. Chen, *J. Appl. Phys.*, **65**, 3610 (1989).
4. J. P. Sinski and E. S. Paight, *Acta Cryst. C*, **51**, 531 (1995).
5. J. P. Christie and C. H. Lui, *Dyes and Pigments*, **42**, 85 (1999).
6. C. W. Tang, S. A. Vansly and C. H. Chen, *J. Appl. Phys.*, **9**, 65 (1989).
7. T. Wakimoto, *Synth. Met.*, **91**, 5 (1997).
8. N. A. H. Male, *Synth. Met.*, **126**, 7 (2002).
9. A. Meyers and M. Weck, *Macromolecules*, **36**, 1766 (2003).
10. J. P. J. Markham, S.-C. Lo, S. W. Magennis, P. L. Burn and I. D. W. Samuel, *Appl. Phys. Lett.*, **80**, 2645 (2002).
11. G. Jones, C. Griffin, C. Y. Bergmank, and W. R. Bergmank, *J. Org. Chem.*, **49**, 2705 (1984).
12. D. M. Mckinnon, P. Spevack and G. Tipples, *Can. J. Chem.*, **66**, 2339 (1998).
13. T. Foster, *Angew. Chem. Int. Ed.*, **8**, 333 (1969).
14. B. Birks, Ed., *Photophysics of Aromatic Molecules*, Wiley, New York, 1970, p. 301.
15. H. Beens and A. Weller, Eds., *Organic Molecular Photophysics*, Vol. 2, Wiley, New York, 1975, p. 59.
16. N. J. Turo, Ed., *Modern Molecular Photochemistry*, Wiley, New York, 1991, pp. 135–148.
17. J. N. Miller, Ed., *Standard in Fluorescence Spectrometry*, Chapman and Hall, New York, 1982, pp. 68–78.