Synthesis and Characterization of Luminescent Poly(ester-imide) Derivatives Constituted of Alternating Spirobifluorene Moiety

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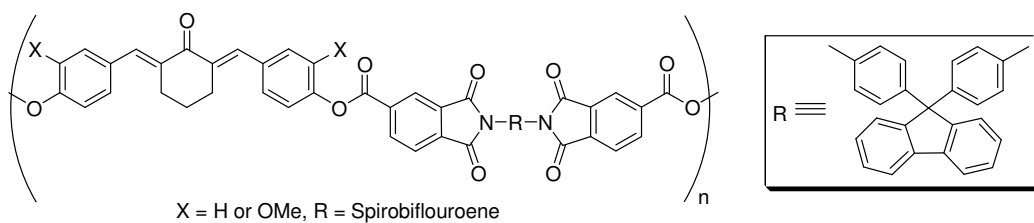Corresponding author. Email: wongfungfuh@yahoo.com.tw, ffwong@mail.cmu.edu.tw

Key words: Conjugated polymers; Spirobiflouroene; Electroluminescence; Poly(ester-imide); Photoluminescence

ABSTRACT

A new category of luminescent poly(ester-imide)s derivatives based on spirobifluorene rings in the main chain was synthesized from 2,6-bis(4-hydroxybenzylidine)cyclohexanone (BC) derivatives and diimide-dicarboxylic acid (DIDA) containing spirobifluorene moiety. The structure of the polymer was confirmed by elemental and spectral analyses. The various characteristics of the resulting polymers including optical properties, solubility, thermal analysis, and X-ray diffraction analysis were determined and discussed. The new polymers showed relatively high glass-transition temperatures (about 200 ℃) and good thermal stability. Two polymers emitted blue-greenish light with

photoluminescence (PL) emission maxima around 400–600 nm and the electron affinity of new polymers was estimated as 2.75–2.84 eV. Cyclic voltammetry displayed that both conjugated polymers had reversible oxidation and irreversible reduction, making them n-type electroluminescent materials.

X = H or OMe, R = Spirobiflouroene

1. Introduction

High-performance polymers have attracted much attention for their excellent thermal stability and solubility to be developed as various thermostable and processable polymers. Among them, poly(ester-imide)s (PEAs) attract scientific interest for they combine the excellent mechanical properties of polyimides and the biodegradability of polyesters [1]. PEAs have a wide range of applications including served as disposable bags, agricultural films, drug carriers, and matrix resins for biomedical materials [2].

Owing to spirobifluorene-based compounds possess the high thermal and morphological stabilities, high fluorescent quantum efficiencies, and anbipolar transporting properties   [3–5], the spiro structure in the spirobifluorene is believed to be effective way to reduce interchain interaction which leads to broadening of emission spectrum [6–8]. As a result, spirobifluorene moiety is considered promising materials for blue light emitting materials in both small molecule and polymer devices [9–11], such as the active component in light emitting diodes, field-effect transistors, photovoltaic cells, and plastic lasers [12]. In this work, we developed new poly(ester-imide)s based on spirobifluorene moiety in the main chain as the electroluminescent materials and provided a facile route for the synthesis and characterization of new poly(ester-imide)s. Two novel oligo-9,9′-spirobifluorene-based poly(ester-imide)s through *para*-linkage are constructed. Furthermore, the characteristics of these two new polymers, such as photophysical properties, thermal stability, solubility, and crystallinity, were discussed. We also reported their photophysical properties and application as host material in phosphorescent organic light-emitting diodes as well as investigated the effect of the inclusion of cyclohexanone moiety on the polymer properties.

2. Experimental

General Procedure. All chemicals were reagent grade and used as purchased. All reactions were carried out under nitrogen atmosphere and monitored by TLC. Flash column chromatography was carried out on silica gel (230–400 mesh). Cyclohexanone, 4-hydroxybenzaldehyde, thionyl chloride, vanillin, *p*-xylene were purchased from Merck Chemical Co. Acetone, boric acid, concentrated hydrochloric acid, *N*-methyl-2-pyrrolidone, and palladium/carbon were purchased from Fluka & Aldrich. Pyridine, trimellitic anhydride, and triphenyl phosphite were purchased from Acros Chemical Co. 9,9'-Bis(4-aminophenyl)fluorine, 3-nitrobenzoic acid, and phosphoryl trichloride were purchased from TCI Chemical Co.

Infrared (IR) spectra were measured on a Bomem Michelson Series FT-IR spectrometer. The wavenumbers reported are referenced to the polystyrene 1601 cm^{-1} absorption. Absorption intensities are recorded by the following abbreviations: s, strong; m, medium; w, weak. UV-visible spectra were measured with a HP 8452A diode-array spectrophotometer. Photoluminescence (PL) spectra were obtained on a Perkin-Elemer fluorescence spectrophotometer (LS 55). Proton NMR spectra were obtained on a Bruker AC-300 (300 MHz) spectrometer by use of DMSO-d_6 as the solvent. Carbon-13 NMR spectra were obtained on a Bruker AC-300 (75 MHz) spectrometer by used of DMSO-d_6 as solvent. Carbon-13 chemical shifts are referenced to the center of the DMSO-d_6 sextet (δ 39.6 ppm). Multiplicities are recorded by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; *J*, coupling constant (hertz).

The UV-VIS spectra of the samples in NMP were measured by a Shimadzu Model UV-160 spectrophotometer. The fluorescence spectra were recorded by a Hitach F-4500 fluorescence spectrometer. Glass transition temperature and thermal gravimetric analyses were performed on a Perkin Elmer Pyris DSC-1 and TGA-7 under a nitrogen stream and with a heating rate of 30 °C/min. X-ray diffraction was measured by Shimadzu X-ray 6000 diffractometer. The current–voltage

characteristics were measured by a Keithely 2400 current/voltage source. All samples were dried in a vacuum oven at 100 °C for 48 h before data taking. All solid thin films of the polymers for optical characterization were prepared by spin coating onto quartz substrates from 3 wt% NMP solution and dried. Elemental analyses were carried out on a Heraeus CHN–O RAPID element analyzer.

Cyclic voltammetry measurements: Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed on a PGSTAT 20 electrochemical analyzer. The oxidation and reduction measurements were carried out, in anhydrous CH_2Cl_2 and THF containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as the supporting electrolyte at a scan rate of 50 mVs^{-1}. The potentials were measured against an Ag/Ag$^+$ (0.01 M AgCl) reference electrode using ferrocene as the internal standard. The onset potentials were determined from the intersection of two tangents drawn at the rising current and background current of the cyclic voltammogram [13].

3. Result and discussion

3.1. Synthesis of 2,6-bis(4-hydroxyarylidene)-cyclohexanone **4** and **5**

Diols 2,6-bis(4-hydroxybenzylidene)-cyclohexanone **4** and 2,6-bis(4-hydroxy-3-methoxybenzylidene)cyclohexanone **5** were synthesized by the method reported by Sakthivel and Kannan [14] and the synthetic route was shown in Scheme 1. To a mixture of 4-hydroxybenzaldehyde (4.9 g, 0.040 mol, 1.0 equiv) or 4-hydroxy-3-methoxybenzaldehyde (6.1 g, 0.040 mol, 1.0 equiv) with boric acid (2.5 g, 0.04 mol, 1.0 equiv.) in a 50 mL round-bottom flask equipped with a mechanical stirrer was added 20 mL of concentrated hydrochloric acid. The reaction mixture was cooled to 0 °C with cooling apparatus and added with cyclohexanone (2.0 g, 0.02 mol, 0.5 1.0 equiv.) was added dropwise in a period of 60 min. The reaction was

continuously stirred at room temperature for 24 h. After the reaction was completed, the mixture was poured into 1.0 L of cooled water and the precipitated blackish green product was filtered and washed with cooled water. Recrystallization was performed from an acetone/water mixture (50:50 v/v). The wet cake dried in vacuum oven for overnight to give the desired product **4** and **5** in 66% and 65% yields, respectively [15].

2,6-Bis(4-hydroxybenzylidene)cyclohexanone (BC, 4): ^{1}H NMR (DMSO-d_6, 300 MHz) δ 1.7 (m, 2 H, γ-CH$_2$), 2.82 (t, 4 H, β-CH$_2$), 6.80–7.39 (m, 8 H, ArH), 7.52 (s, 2 H, CH=), 9.97 (s, 2 H, –OH); IR (pellet, KBr) 3252 (b, OH), 1648 (m, C=O), 1593, 1505 cm^{-1}.

2,6-Bis(vanillylidene)cyclohexanone (BVCH, 5): ^{1}H NMR (DMSO-d_6, 300 MHz) δ 1.70 (m, 2 H, γ-CH$_2$), 2.88 (t, 4 H, β-CH$_2$), 3.80 (s, 6 H, OCH$_3$), 6.83–7.09 (m, 8 H, ArH), 7.54 (s, 2 H, CH=), 9.54 (s, 2 H, –OH); IR (pellet, KBr) 3370 (b, OH), 1639 (m, C=O), 1574, 1515 cm^{-1}.


1
2. X = H
3. X = OMe
4. X = H
5. X = OMe
H$_3$BO$_3$, HCl
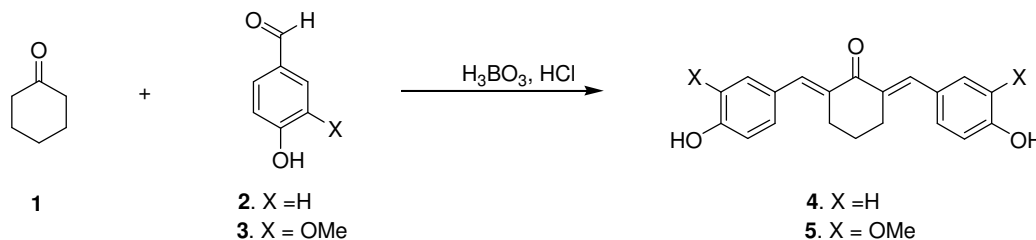
Scheme 1

3.2. Synthesis of diacid chloride 9

The synthetic route of diacid chloride **9** is outlined in Scheme 2. At first, the diacid **8** was synthesized via a one-pot and two-stage procedure involving ring-opening addition and cyclodehydration. 9,9'-Bis(4-aminophenyl)fluorene (**6**, APF, 0.010 mol) and trimellitic anhydride (**7**, TMA, 0.20 mol) were mixed in 30 mL

of dry NMP at room temperature for 12 h. The cyclodehydration condensation was performed by means of xylene–water azeotropic distillation in a Dean–Stark trap [16]. About 5 mL of xylene was then added, and the mixture was heated at the reflux for about 5 h until the water was distilled azeotropically in a Dean–Stark trap. Heating was continued to remove the residual *p*-xylene. After cooling, the residue was precipitated with water to afford the crude product. The crude product was isolated by filtration and purified by recrystallization from NMP. The wet product was dried on a vacuum oven to give the corresponding diimide-dicarboxylic acid **8** in 83% yield: ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.37–8.38 (m, 22 H, Ar-H); IR (pellet, KBr) 3408 (b, OH), 1779 (m, C=O, imide), 1723 (m, C=O, acid), 1373, 732 cm^{-1}. Furthermore, the diacid **8** was successfully converted to the diacid chloride **9** in the presence of SOCl$_2$ (see Scheme 2).
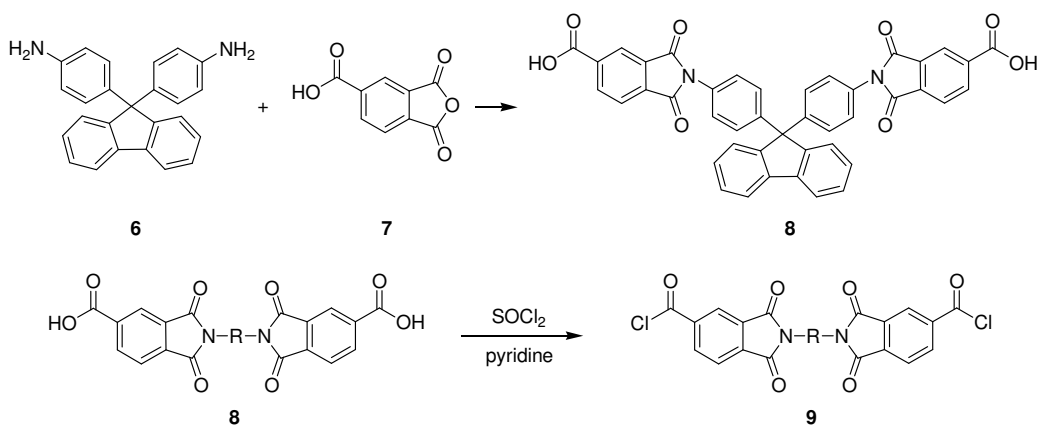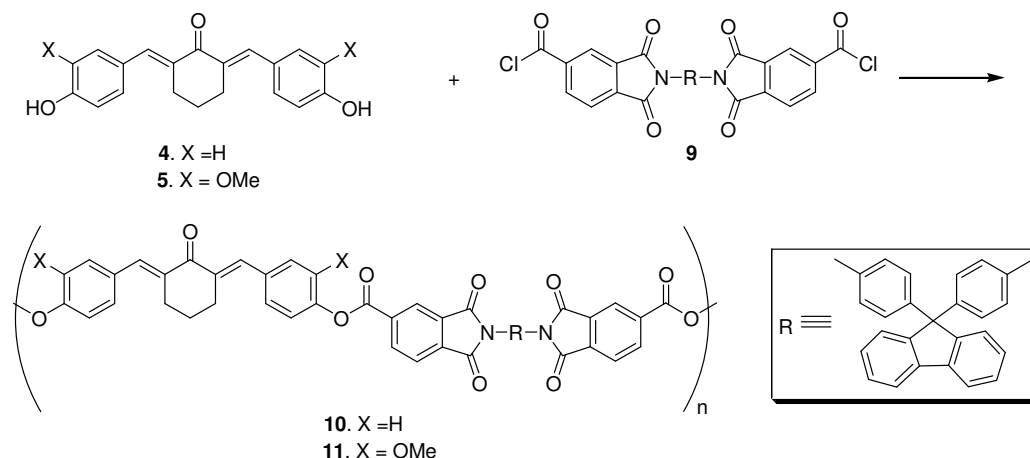

Scheme 2

*3.3. Synthesis of poly(ester-imide)s **10** and **11***

The synthetic route of poly(ester-imide)s **10** and **11** is shown in Scheme 3. A solution of diimide-dicarboxylic acid (**8**, 0.50 mol), thionyl chloride (5.0 mL), and pyridine (5 mL) was heated at reflux for overnight. After the suspension reaction mixture became homogeneous, the solution was concentrated under reduced pressure to remove the

excess thionyl chloride and pyridine. The residue compound was added with fresh pyridine (5.0 mL) and NMP (5.0 mL) under ice-bath and added with 2,6-bis(4-hydroxyarylidene)-cyclohexanones (**4** or **5**, 0.5 mol). After one hour, NMP (0.20 mL) was dropwise added into the reaction mixture for dilution. The resulting solution was stirred at room temperature for 24 h. After the polymerization reaction was completed, 50 mL of water was dropped into the reaction mixture to precipitate the product. The crude product was filtered and washed with cool MeOH/water (10 mL). The wet cake was dried in vacuum oven for overnight to give the desired poly(ester-imide) products (**10** and **11**) in 78–83% yields [17].

Poly(ester-imide)s (10): 1.73 (m, 2 H, γ-CH$_2$), 2.88 (t, 4 H, β-CH$_2$), 6.83–8.61 (m, 32 H, ArH and CH=); IR (pellet, KBr) 1778 (m, C=O, imide), 1724 (m, C=O, acid), 1660, 1598, 1510, 1374, 1205, 1160, 724 cm^{-1}.

Poly(ester-imide)s (11): 1.74 (m, 2 H, γ-CH$_2$), 2.94 (t, 4 H, β-CH$_2$), 3.82 (s, 6 H, OCH$_3$), 6.80–8.63 (m, 30 H, ArH and CH=); IR (pellet, KBr) 1778 (m, C=O, imide), 1724 (m, C=O, acid), 1592, 1512, 1372, 1248, 1206, 1160, 726 cm^{-1}.

4. X =H
5. X = OMe

9

10. X =H
11. X = OMe

Scheme 3

3.4. Optical properties

9,9′-Spirobifluorene derivatives has been known as light emitting materials [18]. However, they have a poor solubility in generally organic solvents according to their high molecular weight. Therefore, the polar solvent NMP was used to dissolve the new poly(ester-imide)s **10** and **11** for the determination their optical properties. Table 1 and Figure 1 show the normalized UV/Vis spectra of 2,6-bis(4-hydroxyarylidene)-cyclohexanone monomers (**4** and **5**) and poly(ester-imide)s (**10** and **11**) in NMP solution. The new spirobifluorene-based poly(ester-imide)s **10** and **11** exhibited very similar UV absorption spectra as shown in Figure 1. They all showed three main strong absorption peaks: one in the visible range at about 355 nm and two peaks in the UV region at 280 nm and 305 nm. Compared to that of 2,6-bis(4-hydroxyarylidene)-cyclohexanone monomers (**4** and **5**, the λ_{max} value is 300 ± 5 nm in NMP solution), the UV absorption peak of the new poly(ester-imide)s (**10** and **11**) is complicate. The new forming visible absorption peak (~350 nm) is assigned to the π–π^* transition of the cross-conjugated spirobifluorene segment, which is confirmed by the same absorption maxima of the monomer (**5a–5b**) [7]. Apparently, the absorption at about ~280 nm was assigned to the π–π^* transition of the imidyl group moiety. The UV-vis absorption peaks of the new polymers **10** and **11** in the film are more complicate and displayed the blue shift.

Table 1. Characterization of the monomers **4** and **5** and spirobifluorene-based poly(ester-imide)s **10** and **11**.

Compounds	Absorbance λ_{max} (Uv-vis, nm)		Emission λ_{max} (PL, nm)
	NMP solution	Film	NMP solution
4	354, 407	-	418, 509
5	383, 412	270, 412, 459	526
10	283, 310, 357	369, 414, 436	498

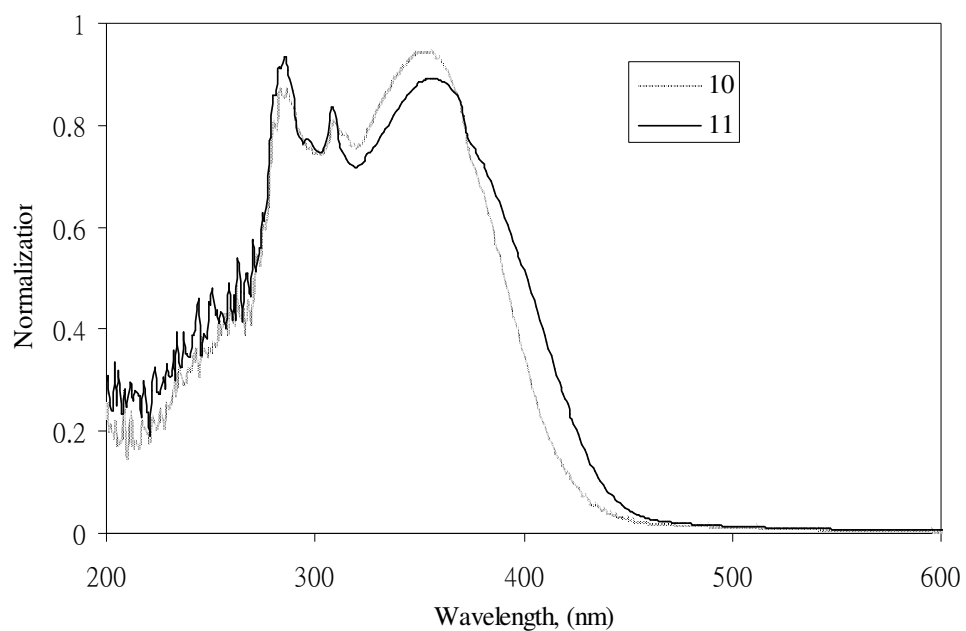| 11	281, 307, 354	371, 399	374, 486

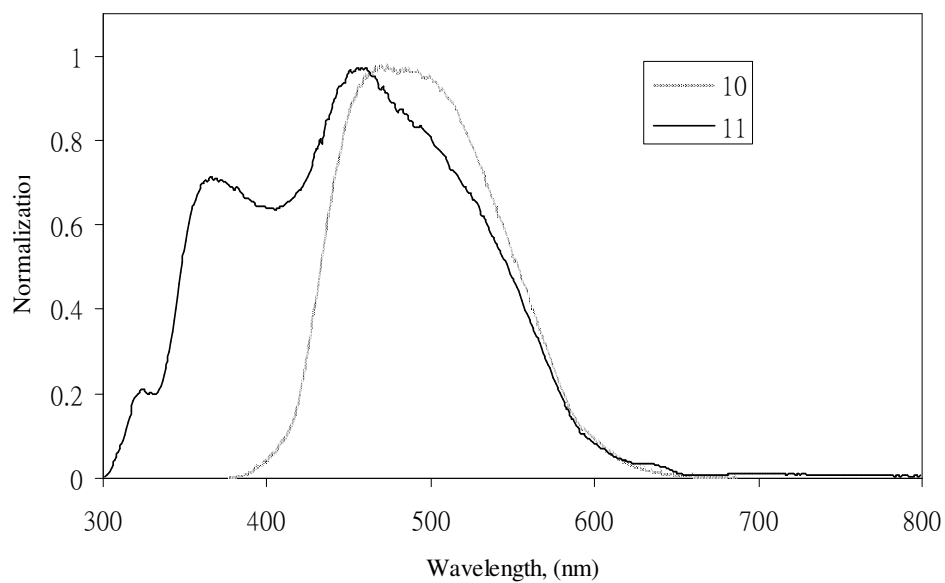**Fig. 1.** The UV-vis Spectra of **10** and **11** in NMP solution.

Fig. 2. The PL Spectra of **10** and **11** in NMP solution.

Table 1 shows the photoluminescence (PL) spectra of

2,6-bis(4-hydroxyarylidene)-cyclohexanone monomers (**4** and **5**) and spirobifluorene-based poly(ester-imide)s (**10** and **11**) in NMP solution. The poly(ester-imide)s **10** and **11** exhibited a broad emission at about 400–600 nm in NMP solution, especially for polymer **11** (about 350–600 nm, see Figure 2). Emissions of the 9,9′-spirobifluorene derivatives [19] at 400–500 nm and the 2,6-bis(4-hydroxyarylidene)-cyclohexanone unit at 450–600 nm are observed (see Figure 2). The absorption spectra of the new spirobifluorene-based poly(ester-imide)s **10** and **11** show almost identical maxima to their absorption spectra, indicating the existence of efficient energy transfer from the 9,9′-spirobifluorene moiety to the 2,6-bis(4-hydroxyarylidene)-cyclohexanone backbone.

3.5. Cyclic Voltammetry Measurements

The electrochemical properties of the new spirobifluorene-based poly(ester-imide)s **10** and **11** were investigated by cyclic voltammetry (see Figures 3 and 4), and the resulting data were summarized in Table 2. Upon the anodic sweep, **10** and **11** showed reversible reduction processes and irreversible oxidation. Compounds **10** and **11** were used as example and shown in Figures 3 and 4. The bandgap energies of spirobifluorene-based poly(ester-imide)s **10** and **11** are estimated from the onset wavelength (λ_{onset}) of the UV-vis absorption [20]. Compounds **10** and **11** have the high LUMO values about ≥ 3.94 eV and the high electron affinities were ≥ 2.75 eV.

Table 2. Electrochemical properties of monomers **4** and **5** and spirobifluorene-based poly(ester-imide)s **10** and **11**.

Compounds	Eonset[a] (V)	E'onset[b] (V)	λ_{onset}	$Ip^{c,f} = E_{HOMO}$ (eV)	$Eg^{d,f} =$ Bandgap energy (eV)	$Ea^{e,j} = E_{LUMO}$ (eV)
4	0.81	1.00	442	6.79	2.80	3.99

5	0.65	0.84	448	6.91	2.77	4.14
10	0.66	0.85	436	6.98	2.84	4.14
11	0.86	1.05	451	6.69	2.75	3.94

[a] Measured vs. ferrocene/ferrocenium.

[b] E'onset = Eonset + 0.19 eV (Measured vs. Ag/AgCl)

[c] Ip = - (E'onset + 4.8)

[d] Eg: the bandgap energy estimated from the onset wavelength of UV-vis absorption and the equation Y = –0.033 * X + 11.141 (X = λ_{onset})

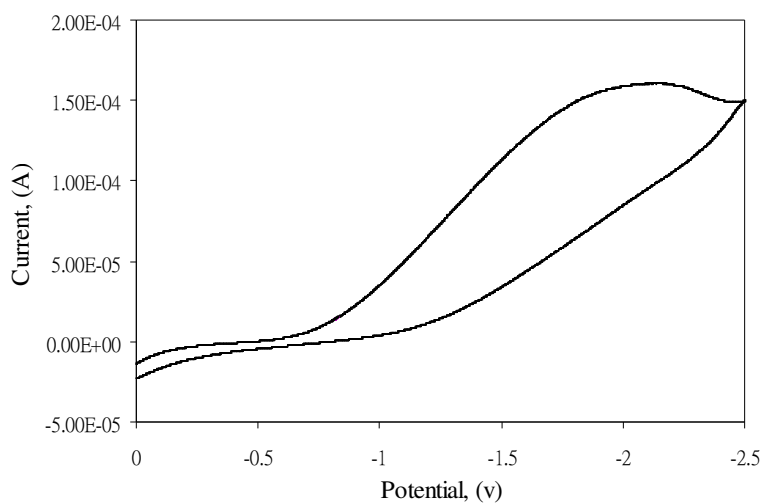[e] $Ea = Ip + Eg$

[f] $1\ eV = 96.5\ kJ/mol$

Fig. 3. Cyclic Voltammetry of spirobifluorene-based poly(ester-imide) **10**.
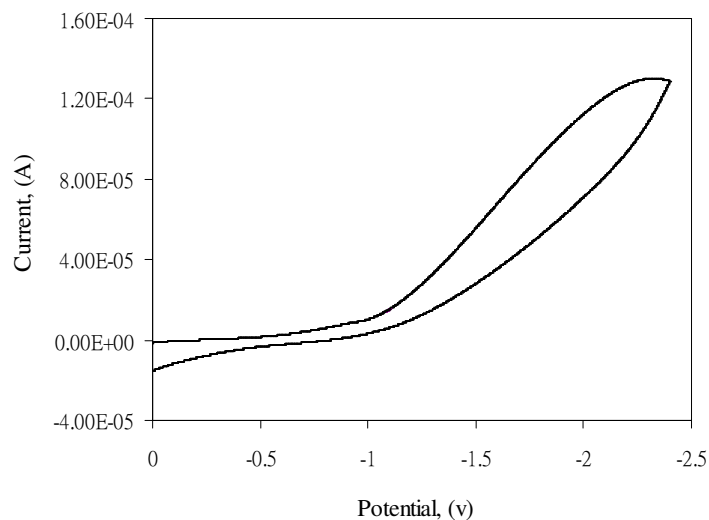

Fig. 4. Cyclic Voltammetry of spirobifluorene-based poly(ester-imide) **11**.

3.5. Thermal properties

Thermal and thermomechanical characterization of the polymers were carried out by DSC and TGA. The glass-transition temperatures (Tg) of the new spirobifluorene-based poly(ester-imide)s **10** and **11** were determined by the DSC method. No phase transitions were recorded during the first and second heating in the DSC experiments. The absence of melting endotherm confirmed the amorphous nature of the polymers. The Tg was obtained from the onset temperature of the first inflection point that was recorded during the second heating (see Table 3, Figure 5). Compounds **11** showed a slightly lower Tg (197 °C) than **10** (204 °C) that was attributed to the presence of the electrodonating group methoxy group in the 2,6-bis(4-hydroxyarylidene)cyclohexanone core backbone. The TGA thermograms of the polymers are summarized in Table 3 and Figure 6. The spirobifluorene-based poly(ester-imide)s **10** and **11** were stabled up to ~200–220 °C in the N_2. They afforded a relatively low anaerobic char yield (ca. 46% and 52%) at 800 °C because of the thermally sensitive methoxyl side groups. Compound **11** was slightly more thermally stable than **10**, and all its thermal properties were promoted by grafting 9,9′-spirobifluorene moiety in main core chain.

Table 3. Tg values and thermal stability of spirobifluorene-based poly(ester-imide)s **10** and **11** (heating and cooling rate: 10 °C/min).

Conjugated polymers	Tg[a] (°C)	T_1[b] (°C)	T_{10}[b] (°C)	Y_c[c] (%)
10	204	188	356	46
11	197	208	364	52

[a] Tg: glass-temperature determined by the DSC method.
[b] T_1, T_{10}: temperature at which weight losses of 1 and 10 %, respectively, were observed by TGA.
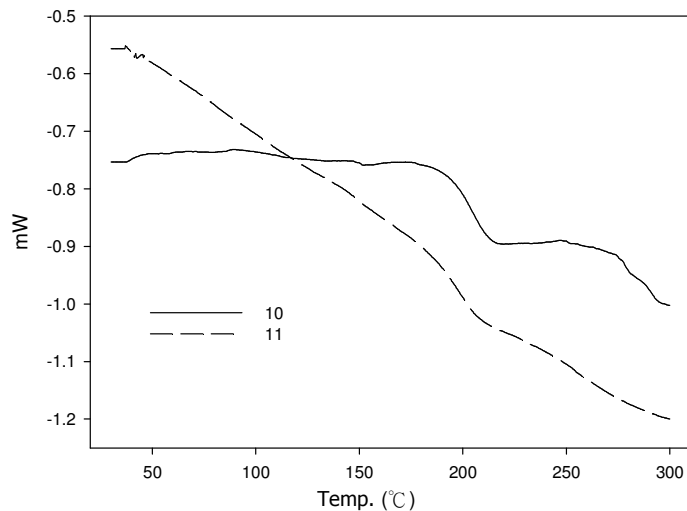[c] Y_c: Char yield at 800 °C by TGA.

Fig. 5. DSC thermograms of the spirobifluorene-based poly(ester-imide)s **10** and **11**
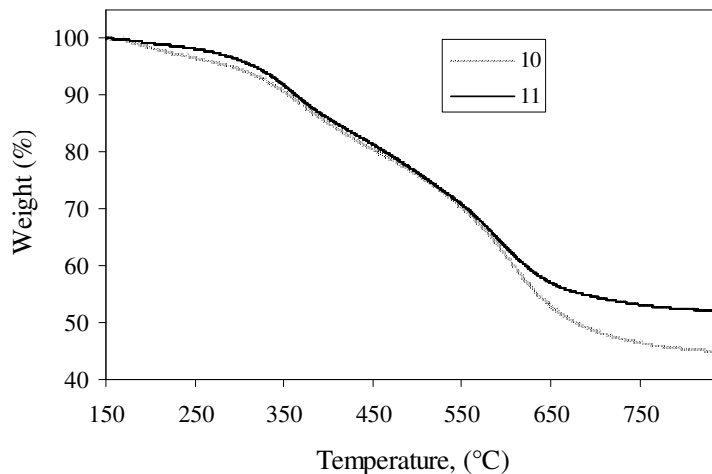

Fig. 6. TGA thermograms of the spirobifluorene-based poly(ester-imide)s **10** and **11**.

3.6. Solubility

Room temperature solubility characterization of spirobifluorene-based poly(ester-imide)s **10** and **11** were tested by using various solvents including acetone, chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), MeOH, EtOH, THF, DMF, DMSO, and NMP. A 5% (w/v) solution was taken as criterion for solubility. Following the resulting data shown in Table 4, the spirobifluorene-based poly(ester-imide)s were

insoluble in most of the organic solvents such as alcohols, acetone, chloroform (CHCl$_3$), dichloromethane (CH$_2$Cl$_2$), and THF. The poly(ester-imide)s **10** and **11** were partially or completely soluble in polar aprotic solvents including DMF, DMSO, and NMP. All the synthesized poly(ester-imide)s were freely soluble and gave reddish color. In comparison with the solubility of the polymers **10** and **11** based on the 2,6-bis(4-hydroxyarylidine)cyclohexanone moieties, polymer **11** was more soluble than polymer **10** in most solvents. This may be attributed to the higher flexibility of methoxy group on 2,6-bis(4-hydroxyarylidine)cyclohexanone moiety.

Table 4. Solubility characterization of the spirobifluorene-based poly(ester-imide)s **10** and **11**.

Polymers	acetone	CH$_2$Cl$_2$	CHCl$_3$	MeOH	EtOH	THF	DMF	DMSO	NMP
10	–	–	–	–	–	–	±	±	+
11	–	–	–	–	–	–	±	±	+

3.7. X-ray analysis

The X-ray diffractiongrams of the spirobifluorene-based poly(ester-imide)s **10** and **11** were shown in Figure 7. It can be clarified from the Fig. 7 that the majority of the new luminescent poly(ester-imide)s **10** and **11** showed few reflection peaks in the region $2\theta = 5$–$40°$, indicating that polymers are semicrystalline and amorphous patterns. This observation is reliable, because the presence of the mentioned bulky spirobifluorene group decreases the intermolecular forces between the polymer chains, causing a decrease in crystallinity. In comparison with polymers **10** and **11**, it was found that the presence of methoxy group in the polymer backbone caused some hindering and enforced it to unsymmetrical orientation in the polymer chain and reduced the crystallinity.
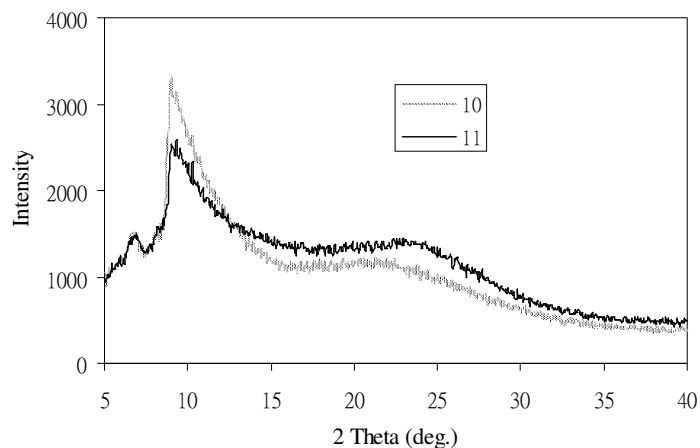
Fig. 7. X-ray diffraction patterns of the spirobifluorene-based poly(ester-imide)s **10** and **11**.

4. Conclusions

Two new poly(ester-imide)s containing cyclohexanone and spirobifluorene moieties in the main core were firstly synthesized as the new n-type electroluminescent materials. The spirobifluorene-based poly(ester-imide)s had moderate Tg (204 and 197 °C) and the good thermal stability. Compound **10** had a higher Tg and electron affinity than **11**. The electron affinity of new polymers was estimated as 2.75–2.84 eV. The poly(ester-imide)s were emitted blue-greenish light with PL emission maxima around 400–600 nm in NMP solution or thin film. Cyclic voltammetry displayed that both poly(ester-imide)s had reversible reduction and irreversible oxidation, making them n-type electroluminescent materials.

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Synthesis and Characterization of Luminescent Poly(ester-imide) Derivatives Constituted of Alternating Spirobifluorene Moiety

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A new category of luminescent poly(ester-imide)s derivatives based on spirobifluorene rings in the main chain was synthesized from 2,6-bis(4-hydroxybenzylidine)cyclohexanone (BC) derivatives and diimide-dicarboxylic acid (DIDA) containing spirobifluorene moiety. The structure of the polymer was confirmed by elemental and spectral analyses. The various characteristics of the resulting polymers including optical properties, solubility, thermal analysis, and X-ray diffraction analysis were determined and discussed. The new polymers showed relatively high glass-transition temperatures (about 200 °C) and good thermal stability. Two polymers emitted blue-greenish light with photoluminescence (PL) emission maxima around 400–600 nm and the electron affinity of new polymers was estimated as 2.75–2.84 eV. Cyclic voltammetry displayed that both conjugated polymers had reversible oxidation and irreversible reduction, making them n-type electroluminescent materials.

X = H or OMe, R = Spirobiflouroene

R ≡