

# Silole-Containing Poly(diphenylacetylene): Synthesis, Characterization, and Light Emission

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**ABSTRACT:** A disubstituted polyacetylene consisting of a poly(diphenylacetylene) backbone and a 1,2,3,4,5-pentaphenylsilole ( $\text{SiC}_4\text{Ph}_5$ ) pendant, that is,  $-\{(\text{C}_6\text{H}_5)\text{C}=\text{C}[\text{C}_6\text{H}_4\text{O}(\text{CH}_2)_3\text{C}\equiv\text{CSiC}_4\text{Ph}_5]\}_n-$  (PS3DPA), was synthesized, and its light emission from both the backbone and the pendant was evaluated. The polymerization of  $\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_4\text{O}(\text{CH}_2)_3\text{C}\equiv\text{CSiC}_4\text{Ph}_5$  with two ethynyl groups was effected with  $\text{WCl}_6\text{-Ph}_4\text{Sn}$  as the catalyst. The structure and properties of PS3DPA were characterized and evaluated by IR, UV, NMR, thermogravimetric analysis, differential scanning calorimetry, photoluminescence, and electroluminescence analyses. The ethynyl group of the diphenylacetylene moiety was polymerized exclusively, giving a soluble PS3DPA. The chloroform solution of PS3DPA showed a backbone emission that peaked at 522 nm, whereas the silole pendant was nonradiative at room temperature. The polymer did not show the aggregation-induced emission phenomenon, probably because the silole clusters were difficult to form when the polymer chains aggregated because of the very high rigidity of the main chain. Intramolecular rotations of the phenyl groups of the silole moieties were responsible for the nonradiative decay of the silole chromophore. The intramolecular rotations, however, could be largely restricted in a cooling process of the polymer solution, showing cooling-enhanced emission. The silole emission became dominant at lower temperatures. A multilayer electroluminescence device based on PS3DPA emitted a green light that peaked at 512 nm. © 2006 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 44: 2487–2498, 2006

**Keywords:** conjugated polymers; light-emitting diodes (LED); luminescence; polyacetylenes

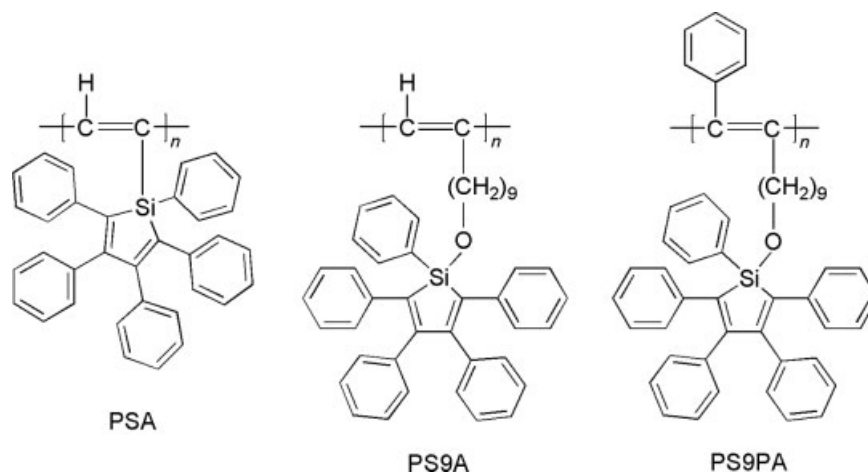
## INTRODUCTION

Siloles or silacyclopentadienes possess a unique  $\sigma^*-\pi^*$  conjugation that significantly lowers their lowest unoccupied molecular orbital energy levels and increases their electron affinities.<sup>1</sup> Siloles show intriguing aggregation-induced emissions

(AIEs), being almost nonluminescent in solutions but highly emissive in the solid state.<sup>2,3</sup> The photoluminescence (PL) quantum yields ( $\Phi_{\text{PL}}$ ) of the aggregates of siloles can differ from that of their molecularly dissolved species by 2 orders of magnitude. Siloles also show cooling-enhanced emission (CEE): PL of a silole solution increases with a decrease in the temperature.<sup>3</sup> Restricted intramolecular rotations have been proposed as a model for the mechanism of the AIE and CEE behaviors.<sup>3,4</sup> Because of their high electron affin-

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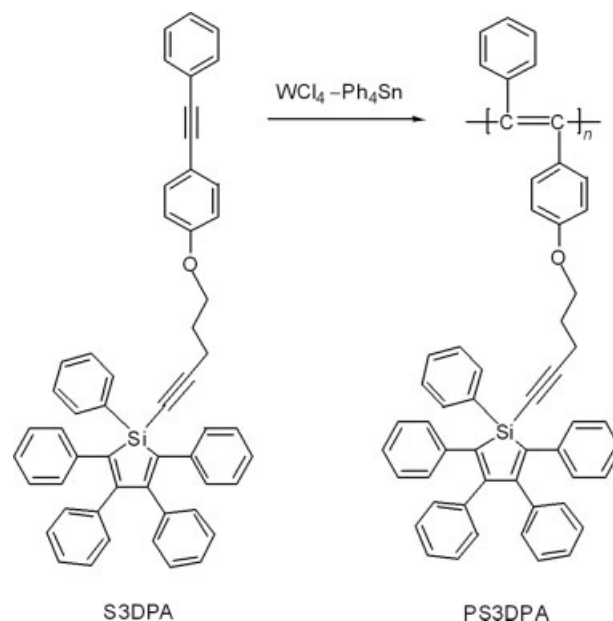


**Chart 1.** Molecular structures of PSA, PS9A, and PS9PA.

ities and excimer-free AIE attributes,<sup>5</sup> siloles have been used as electron-transporting<sup>6–8</sup> and light-emitting layers<sup>9–16</sup> in the fabrications of highly efficient electroluminescence (EL) devices. There have been great efforts to incorporate siloles into polymers because polymers possess processing advantage over their small-molecule counterparts.<sup>17–29</sup> Silolyl polymers, such as poly(2,5-silole),<sup>17</sup> poly(1,1-silole),<sup>18</sup> silole–thiophene copolymers,<sup>19</sup> silole–fluorene copolymers,<sup>20–22</sup> silole–carbazole copolymers,<sup>23</sup> poly(dithienosilole),<sup>24</sup> silole–acetylene copolymers,<sup>25</sup> silole–silane copolymers,<sup>26</sup> silole side-chain polymers,<sup>27</sup> hyperbranched polysiloles,<sup>28</sup> and silole-cored dendrimers,<sup>29</sup> have been reported. Device applications, such as light-emitting diodes,<sup>20–24,27</sup> photovoltaic cells,<sup>21</sup> and field effect transistors,<sup>21,23</sup> have been demonstrated.

Polyacetylene is an important electroactive polymer but is notorious for its instability and intractability.<sup>30</sup> Replacements of one or two hydrogen atoms in the repeat unit of the polymer by one or two substituents give rise to mono- or disubstituted polyacetylenes, respectively, which can be stable, processable, and functionalizable.<sup>31–41</sup> Compared with its monosubstituted counterpart, a disubstituted polyacetylene shows such advantages as being thermally more stable, better at film forming, and mechanically much stronger.<sup>42–46</sup> Although polyacetylene itself is not luminescent, recent studies have revealed that its substituted derivatives can be emissive,<sup>46–50</sup> with disubstituted polyacetylenes being generally more luminescent than their monosubstituted counterparts.<sup>27,51–55</sup> Among disubstituted polyacetylenes, poly(1-phenyl-1-alkyne)s and poly(diphenylacetylene)s (PDPAs) are typical examples of highly luminescent polyacetylenes.<sup>56–59</sup> We are interested in

the chemistry of acetylene polymerization to incorporate siloles into polyacetylenes. In our previous work, we synthesized three silole-containing polyacetylenes (PSA, PS9A, and PS9PA; Chart 1).<sup>27</sup> PS9A and PS9PA were the first examples of AIE-active polymers, showing silole-dominant emissions when aggregates of the polymers were formed, whereas no silole emission could be observed for PSA aggregates, possibly because of the excitation energy transfer from the silole pendant to the polyene backbone. Here we report the synthesis and properties of a silole-containing PDPA, poly(1-phenyl-2-*p*[[1,2,3,4,5-pentaphenylsilyloxy]-5-pentyloxy]phenyl]acetylene) (PS3DPA; Scheme 1). Its mono-



**Scheme 1.** Synthesis of PS3DPA.

mer, 1-phenyl-2- $\{p$ -[(1,2,3,4,5-pentaphenylsilyloxy)-5-pentynyl]oxy]phenyl]acetylene (S3DPA), carries two ethynyl groups. However, the ethynyl group of the diphenylacetylene moiety could be polymerized exclusively with  $WCl_6$ - $Ph_4Sn$  as the catalyst, giving a soluble PS3DPA. The structure and properties of PS3DPA were characterized and evaluated by IR, UV, NMR, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), PL, and EL analyses.

## EXPERIMENTAL

### Materials

Tetrahydrofuran (THF), dioxane, and toluene (all from Lab-Scan) were predried over 4-Å molecular sieves and distilled from sodium benzophenone ketyl immediately before use. Triethylamine (RdH) was dried and distilled over KOH. Trichlorophenylsilane, dichlorobis(triphenylphosphine) palladium(II), 5-chloropentyne, phenylacetylene, 4-iodophenol, copper(I) iodide, lithium wire, butyllithium (2.5 M in *n*-hexane), tungsten(VI) chloride, niobium(V) chloride, tantalum(V) chloride, and tetraphenyltin were all purchased from Aldrich and used without further purification.

### Instrumentation

The  $^1H$  and  $^{13}C$  NMR spectra were obtained on a Bruker ARX 300 or Varian Mercury 300 spectrometer with tetramethylsilane (TMS) as the internal reference. The weight-average and number-average molecular weights ( $M_w$  and  $M_n$ , respectively) of the polymers were estimated with a Waters 510 gel permeation chromatograph. Degassed THF was used as an eluent at a flow rate of 1.0 mL/min. A set of 12 monodisperse polystyrene standards covering a molecular weight range of  $10^2$  to  $10^7$  were used for the molecular weight calibration. The IR spectra were recorded on a PerkinElmer 16 PC Fourier transform infrared spectrometer. The mass spectroscopy (MS) was measured on a Finnigan TSQ 7000 triple quadrupole mass spectrometer operating in a chemical ionization (CI) mode, with methane as the carrier gas. The UV absorption spectra were recorded on a Milton Roy Spectronic 3000 array spectrophotometer, and the molar absorptivity ( $\epsilon$ ) of the polymer was calculated on the basis of its monomer repeat unit. The thermal transition of the polymer was investigated with a Setaram DSC 92 differential scanning calorimeter under

nitrogen at a scanning rate of 5 °C/min, and the thermal stability was evaluated on a Perkin-Elmer TGA 7 thermogravimetric analyzer under nitrogen at a heating rate of 20 °C/min.

All the PL spectra of the polymer solutions and the aggregate suspensions were recorded on an SLM 8000C spectrofluorometer. The sample chamber of the spectrofluorometer was dehumidified with  $P_2O_5$ . The aggregate suspensions were freshly prepared by the addition of poor solvents to the solutions of the polymers in their good solvents with vigorous shaking. For example, a suspension of nanoparticles of PS3DPA was prepared by the addition of 8 mL of methanol to 2 mL of a chloroform solution of PS3DPA in a 10-mL volumetric flask. The concentrations of all the aggregate suspensions were adjusted to  $1 \times 10^{-5}$  mol/L. The EL spectra were obtained on a Kollmorgen Instrument PR650 photospectrometer.

### Monomer Synthesis

Monomer S3DPA was prepared by the reaction of a pentynyllithium (**3**) with a chlorosilole [1-chloro-1,2,3,4,5-pentaphenylsilole (**4**); Scheme 2]. The detailed experimental procedures for the synthesis of the diphenylacetylene (DPA) monomer are given next.

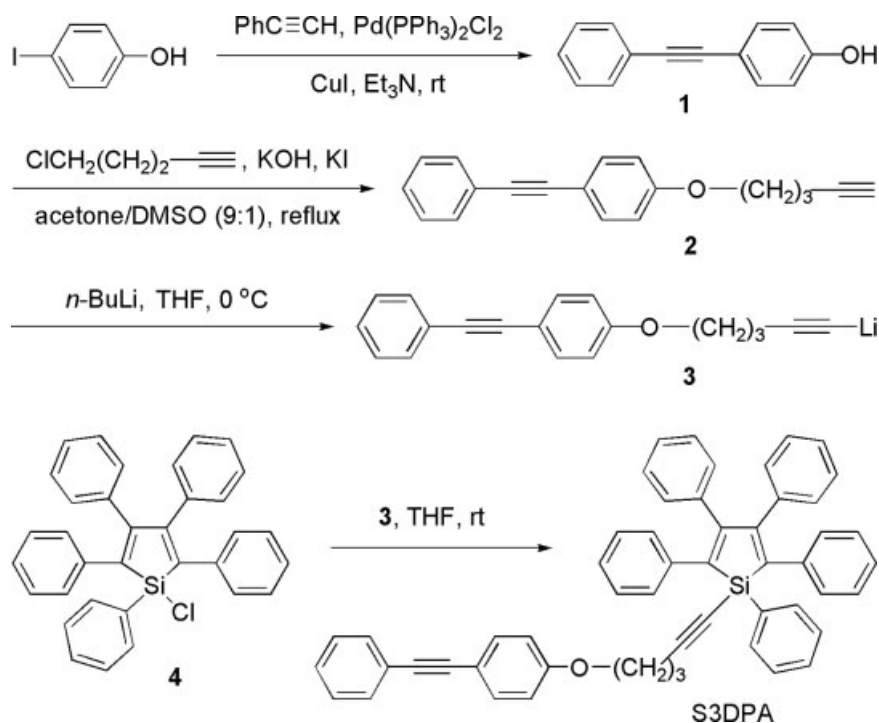
#### 1-Phenyl-2-(*p*-hydroxyphenyl)acetylene (**1**)

Into a 250-mL, round-bottom flask were added copper(I) iodide (3 mg, 16  $\mu$ mol), dichlorobis(triphenylphosphine)palladium(II) (0.42 g, 0.6 mmol), 4-iodophenol (6.6 g, 30 mmol), and phenylacetylene (6.6 mL, 60 mmol) in 100 mL of triethylamine. The mixture was stirred for 24 h at room temperature. After the filtration and removal of the solvent, the crude product was purified on a silica-gel column with a chloroform/acetone mixture (10:1 v/v) as the eluent. A light brownish solid was obtained in an 88% yield.

IR (KBr,  $\nu$ ,  $cm^{-1}$ ): 2220 (C $\equiv$ C stretching).  $^1H$  NMR (300 MHz,  $CDCl_3$ ,  $\delta$ , TMS, ppm): 7.50 (m, 2H), 7.42 (d,  $J = 8.77$  Hz, 2H), 7.32 (m, 3H), 6.79 (d,  $J = 8.77$  Hz, 2H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ,  $\delta$ , TMS, ppm): 155.6, 133.2, 131.4, 128.3, 128.0, 123.4, 115.6, 115.5, 89.2, 88.1.

#### 1-Phenyl-2-[*p*-(5-pentynyl)oxy]phenyl]acetylene (**2**)

To a 250-mL, flat-bottom flask equipped with a condenser were added **1** (4.85 g, 25 mmol), potassium hydroxide (1.54 g, 27.5 mmol), potassium



**Scheme 2.** Synthetic procedures for monomer S3DPA.

iodide (5 g, 30 mmol), and 5-chloropentyne (2.82 g, 27.5 mmol) in 100 mL of an acetone/dimethyl sulfoxide (DMSO) mixture (9:1 v/v). The mixture was refluxed for 24 h. After the filtration and removal of the solvent, the crude product was purified on a silica-gel column with chloroform as the eluent. A white crystal was obtained in an 83% yield.

IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3270 ( $\equiv\text{C}-\text{H}$  stretching), 2217 ( $\text{C}\equiv\text{C}$  stretching).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ , TMS, ppm): 7.50 (m, 2H), 7.45 (d,  $J = 8.77$  Hz, 2H), 7.31 (m, 3H), 6.86 (d,  $J = 8.77$  Hz, 2H), 4.05 (t,  $J = 6.10$  Hz, 2H), 2.38 (m, 2H), 1.99 (m, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ,  $\delta$ , TMS, ppm): 158.9, 133.0, 131.4, 128.3, 127.9, 123.6, 115.4, 114.5, 89.4, 88.0, 83.3, 69.0, 66.1, 28.0, 15.1.

#### 1-Chloro-1,2,3,4,5-pentaphenylsilole (4)

Under pure and dry nitrogen, 180 mg of fresh lithium shavings (25.9 mmol) was added to a solution of diphenylacetylene or tolan (6 g, 33.6 mmol) in 25 mL of THF. The mixture was stirred for 12 h at room temperature and then added dropwise to a solution of trichlorophenylsilane (1.86 mL, 11.6 mmol) in 120 mL of THF. The resultant solution was refluxed for 5 h, and this gave the desired product (4). The THF solution of reactive

intermediate 4 was used *in situ* for the synthesis of monomer S3DPA without isolation.

#### 1-Phenyl-2-[p-[(1,2,3,4,5-pentaphenylsilyloxy)phenyl]acetylene]acetylene (S3DPA)

To a 100-mL, round-bottom flask under nitrogen were added THF (10 mL) and 2 (3.02 g, 11.6 mmol). Cooled by an ice-water bath, *n*-butyllithium (2.5 M in *n*-hexane; 4.65 mL, 11.6 mmol) was dropwise added to the flask. The mixture was stirred for 0.5 h, and this gave the desired product (3). The resultant mixture was added dropwise to a mixture of 4. After stirring for 2 h, the mixture was filtered, and the crude product was purified on a silica-gel column with an *n*-hexane/chloroform mixture (2:1 v/v) as the eluent to afford 3.88 g of S3DPA (yellow-greenish solid) in a 46% yield (based on trichlorophenylsilane).

IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 2215, 2174 ( $\text{C}\equiv\text{C}$  stretching).  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $\delta$ , TMS, ppm): 7.83 (m, 2H), 7.56–7.36 (m, 10H), 7.11–7.03 (m, 16H), 6.91 (m, 6H), 4.08 (t,  $J = 6.10$  Hz, 2H), 2.67 (t,  $J = 6.86$  Hz, 2H), 2.10 (m, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $\delta$ , TMS, ppm): 159.5, 157.2, 139.2, 138.6, 137.8, 135.3, 133.4, 131.7, 131.3, 130.8, 130.1, 129.5, 128.8, 128.7, 128.4, 128.2, 128.0, 127.0, 126.4, 124.0, 115.7, 115.0, 113.1, 89.7, 88.3, 77.4, 66.5, 28.4, 17.4. MS (CI):  $m/e$  721 [(M + 1) $^+$ ].

UV ( $\text{CHCl}_3$ ,  $1 \times 10^{-5}$  mol/L),  $\lambda_{\text{max}}$  (nm)/ $\epsilon_{\text{max}}$  ( $\text{mol}^{-1} \text{L cm}^{-1}$ ): 291/3.91  $\times 10^4$ , 310/3.02  $\times 10^4$ , 374/9.31  $\times 10^3$ .

### Polymerization

All the polymerization reactions and manipulations were carried out under dry nitrogen with a standard Schlenk technique in a vacuum line system or an inert-atmosphere glovebox (Vacuum Atmospheres), except for the purification of the polymers, which was conducted in open air. A typical procedure for the polymerization of S3DPA is given next as an example.

To a thoroughly baked and moisture-excluded Schlenk tube with a stopcock in the sidearm was added 144 mg (0.2 mmol) of S3DPA. The tube was evacuated *in vacuo* and then flushed with dry nitrogen three times through the sidearm. Freshly distilled toluene (1 mL) was injected into the tube to dissolve the monomer. A catalyst solution was prepared in another tube by the dissolution of 7.9 mg of tungsten(VI) chloride and 8.5 mg of tetraphenyltin in 1 mL of toluene. The two tubes were aged at 80 °C for 15 min, and the monomer solution was then transferred to the catalyst solution with a hypodermic syringe. The polymerization mixture was stirred at 80 °C under nitrogen for 24 h. The solution was then cooled to room temperature and added dropwise to 350 mL of methanol under stirring via a cotton filter. The precipitate was allowed to stand overnight and was then filtered with a Gooch crucible. The polymer was dried in a vacuum oven to a constant weight. A yellow-greenish powder was obtained in a 56% yield.

Gel permeation chromatography (GPC):  $M_w$  = 4810;  $M_w/M_n$  = 1.7. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 2173 (C≡C stretching).  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $\delta$ , TMS, ppm): 7.96 (2H), 7.46 (6H), 7.18–7.07 (br, 26H), 3.90 (2H), 2.64 (2H), 2.06 (2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $\delta$ , TMS, ppm): 157.0, 139.0, 138.7, 137.7, 135.1, 134.6, 134.3, 131.6, 131.2, 131.1, 130.7, 130.4, 130.2, 130.0, 129.4, 128.7, 128.1, 127.9, 127.4, 126.9, 126.3, 114.9, 113.4, 113.0, 77.0, 66.5, 28.6, 17.5. UV ( $\text{CHCl}_3$ ,  $1 \times 10^{-5}$  mol/L),  $\lambda_{\text{max}}$  (nm)/ $\epsilon_{\text{max}}$  ( $\text{mol}^{-1} \text{L cm}^{-1}$ ): 245/3.86  $\times 10^4$ , 369/1.17  $\times 10^4$ .

### Device Fabrication

A thin, solid film of the polymer was prepared via spin coating from its chloroform solution (5 mg/mL). A multilayer device of indium tin oxide

(ITO)/[1:4 PS3DPA/poly(9-vinylcarbazole) (PVK)]/bathocuproine (BCP)/aluminum 8-hydroxyquinolate ( $\text{Alq}_3$ )/LiF/Al was constructed with PVK as a hole-transporting material and BCP,  $\text{Alq}_3$ , and LiF as hole-blocking, electron-transporting, and electron-injection layers, respectively. The sheet resistance of the ITO glass was 10–20  $\Omega$ /square. The thickness of the PS3DPA/PVK blend film was 50 nm. The layers of BCP (22 nm),  $\text{Alq}_3$  (20 nm), LiF (1.0 nm), and Al (118 nm) were deposited under a vacuum of  $1 \times 10^{-6}$  Torr. The EL area was 12.6  $\text{mm}^2$ .

## RESULTS AND DISCUSSION

### Monomer Synthesis

The silolyldiphenylacetylene monomer S3DPA was prepared by the synthetic route shown in Scheme 2. The palladium-catalyzed coupling of 4-iodophenol with phenylacetylene in triethylamine readily afforded **1** in a good yield. Compound **1** showed a weak IR absorption at 2220  $\text{cm}^{-1}$  corresponding to its C≡C stretching. Compound **2** was prepared in a good yield by the condensation of **1** with 5-chloropentyne in a basic medium. Compound **2** showed two strong IR absorption bands at 3270 (for ≡C–H stretching) and 2217  $\text{cm}^{-1}$  (for the combined C≡C stretching of the two ethynyl groups).

**4** was prepared according to a published procedure, with tolan as a starting material.<sup>3</sup> Compound **4** was used *in situ* without isolation. **3** was prepared by the reaction of **2** with *n*-butyllithium, whose reaction with **4** gave monomer S3DPA in a moderate yield. The silolyl group was introduced into the monomer through a Si–C linkage, which was more stable than the previously reported Si–O–C linkage in PS9A or PS9PA.<sup>27</sup> The IR spectrum of the monomer showed a weak C≡C stretching vibration at 2215  $\text{cm}^{-1}$  for the ethynyl group of the tolan moiety and a much stronger C≡C stretching vibration at 2174 for the pentynyl group connecting the silolyl group. The  $^{13}\text{C}$  NMR spectrum of S3DPA showed two peaks at 113.1 and 77.4 ppm for the ethynyl group connecting the silolyl group and another set of two peaks at 89.7 and 88.3 ppm for the ethynyl group of the tolan moiety. The spectroscopic characterization gave satisfactory data corresponding to the expected structure of S3DPA (see the Experimental section for details).

**Table 1.** Polymerization of S3DPA<sup>a</sup>

No.	Catalyst	Solvent	Temperature (°C)	Yield (%)	$M_w^b$	$M_w/M_n^b$
1	TaCl <sub>5</sub> -Ph <sub>4</sub> Sn	Toluene	Room temperature	0		
2	TaCl <sub>5</sub> -Ph <sub>4</sub> Sn	Toluene	60	0		
3	NbCl <sub>5</sub> -Ph <sub>4</sub> Sn	Toluene	60	23	1430	1.2
4	NbCl <sub>5</sub> -Ph <sub>4</sub> Sn	Toluene	80	26	1430	1.4
5	WCl <sub>6</sub> -Ph <sub>4</sub> Sn	Toluene	60	23	5010	1.5
6	WCl <sub>6</sub> -Ph <sub>4</sub> Sn	Toluene	80	56	4810	1.7
7	WCl <sub>6</sub> -Ph <sub>4</sub> Sn	Toluene	100	26	4790	1.8
8	WCl <sub>6</sub> -Ph <sub>4</sub> Sn	Dioxane	60	0		
9	WCl <sub>6</sub> -Ph <sub>4</sub> Sn	Dioxane	80	0		

<sup>a</sup> Carried out under nitrogen for 24 h ( $[M]_0 = 0.1$  mol/L,  $[Catalyst] = [Cocatalyst] = 0.01$  mol/L).

<sup>b</sup> Estimated by GPC in THF on the basis of polystyrene calibration.

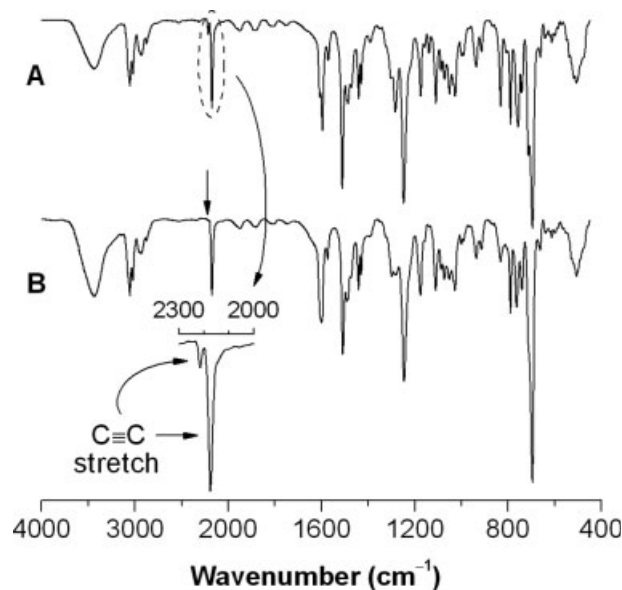
### Polymerization

It has been reported that TaCl<sub>5</sub> is an effective catalyst for the polymerizations of some silicon-containing diphenylacetylenes.<sup>60</sup> We first tried to polymerize S3DPA at room temperature with TaCl<sub>5</sub> as the catalyst and Ph<sub>4</sub>Sn as the cocatalyst. The reaction, however, yielded no polymeric product (Table 1, no. 1). Increasing the polymerization temperature to 60 °C did not help. Taking into consideration the good activities of NbCl<sub>5</sub> and WCl<sub>6</sub> in polymerizing some acetylene monomers carrying silole groups,<sup>27</sup> we tried to use the two catalysts to polymerize S3DPA. Although NbCl<sub>5</sub>-Ph<sub>4</sub>Sn initiated the polymerization of S3DPA, the results at 60 and 80 °C were poor: both the polymer yields and molecular weights were low. The attempt to polymerize S3DPA by WCl<sub>6</sub>-Ph<sub>4</sub>Sn in toluene at 60 °C resulted in the formation of PS3DPA with a molecular weight of 5010. The yield, however, was still low. The polymerization at a higher temperature (80 °C) increased the yield to 56% (Table 1, no. 6). Further increasing the temperature to 100 °C decreased the yield greatly but did not alter the molecular weight much. The attempts to polymerize S3DPA by WCl<sub>6</sub>-Ph<sub>4</sub>Sn in dioxane were unsuccessful. Although S3DPA contains two ethynyl groups, all the products were soluble in common solvents such as chloroform, dichloromethane, and toluene, and this was suggestive of the noncrosslinking nature of the polymers.

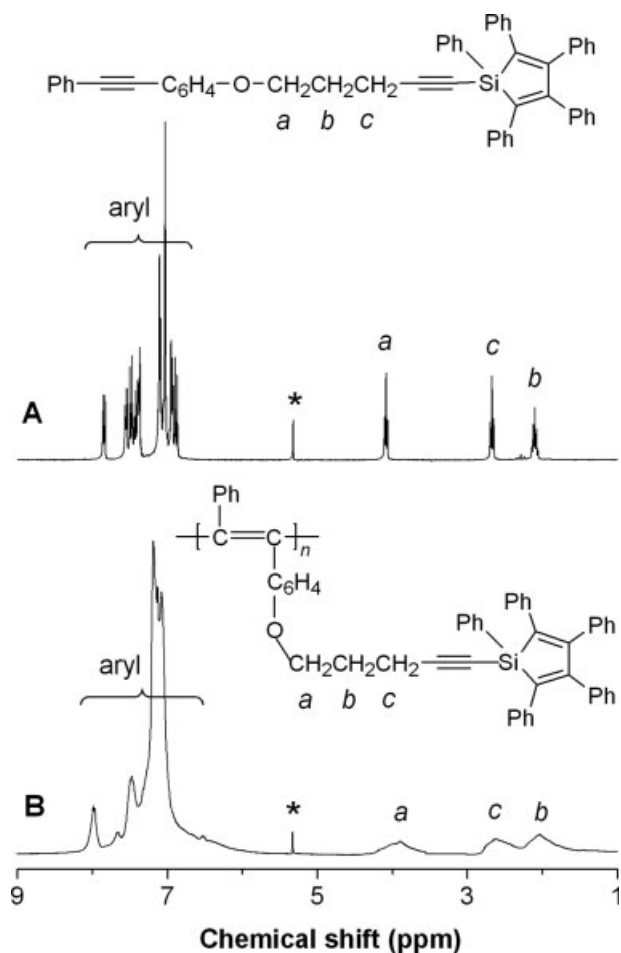
### Structural Characterization

Because S3DPA contains two ethynyl groups, it is necessary to elucidate which ethynyl group has been polymerized. The IR spectrum of PS3DPA is

shown in Figure 1; the spectrum of its monomer S3DPA is also shown in the same figure for comparison. As can be seen from the spectrum of S3DPA, there are two C≡C stretching vibrations at 2215 and 2174 cm<sup>-1</sup>. After polymerization, the absorption at 2215 cm<sup>-1</sup>, attributed to the ethynyl group of the tolan moiety, disappears, whereas the absorption at 2174 cm<sup>-1</sup> for the ethynyl group connecting the silolyl group does not change. Thus, WCl<sub>6</sub> initiated the polymerization of the ethynyl group of the tolan moiety exclusively, giving a silole-containing PDPA. The polymerization products with NbCl<sub>5</sub> as the catalyst showed the same change in the IR spectra. The ethynyl group connecting the silole ring was inactive in the



**Figure 1.** IR spectra of (A) S3DPA and (B) PS3DPA (sample from Table 1, no. 6).



**Figure 2.**  $^1\text{H}$  NMR spectra of (A) S3DPA and (B) PS3DPA (sample from Table 1, no. 6) in  $\text{CD}_2\text{Cl}_2$  (the asterisk indicates the solvent peak).

polymerization, possibly because of the steric and electronic effects of the pentaphenylsilolyl group.

As can be seen from Figure 2, the  $^1\text{H}$  NMR spectrum of PS3DPA resembles that of its monomer S3DPA. In the  $^{13}\text{C}$  NMR spectrum of S3DPA (Fig. 3), there exist four acetylenic carbon resonances at  $\delta$  89.7 and 88.3 ppm for the ethynyl group of the tolan moiety and at  $\delta$  113.1 and 77.4 ppm for the ethynyl group connecting the silolyl group. The peaks at 89.7 and 88.3 ppm disappear in the spectrum of PS3DPA, whereas the peaks for the ethynyl group connecting the silolyl group still exist, confirming the finding by IR analysis; that is, PS3DPA is a PDPA derivative.

### Thermal Properties

Figure 4 shows the TGA and DSC thermograms of PS3DPA. The polymer lost almost no weight when heated to a temperature of  $\sim 300$   $^\circ\text{C}$ . The

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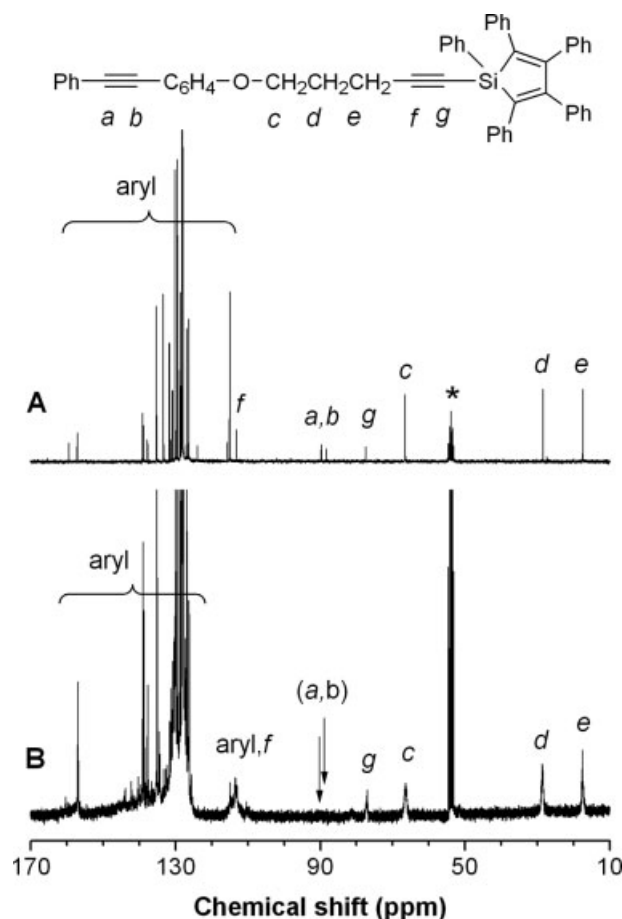
temperature for 5% weight loss was 399  $^\circ\text{C}$ , indicating that the polymer was thermally fairly stable.<sup>60</sup> The DSC thermogram of PS3DPA exhibited no detectable signals corresponding to a glass transition from room temperature up to 300  $^\circ\text{C}$  because of the high rigidity of the PDPA backbone of PS3DPA.<sup>61</sup>

### UV Absorption

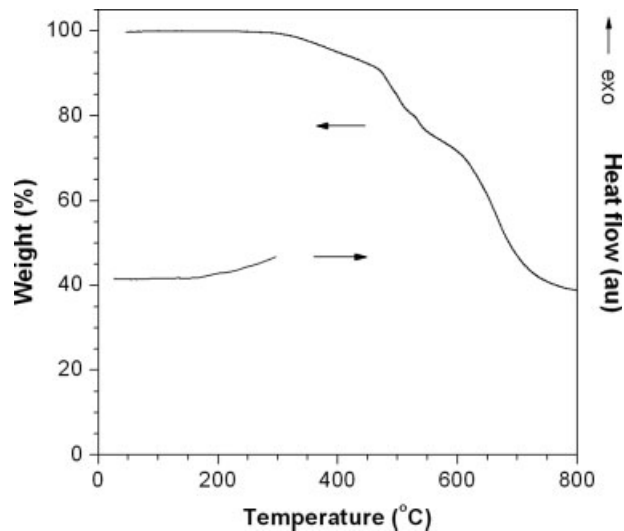
Figure 5 shows the UV absorption spectra of PS3DPA and S3DPA in chloroform. S3DPA exhibited a peak at 374 nm due to the absorption of its silole moiety. PS3DPA showed a higher  $\epsilon$  value because of the additional absorption by the PDPA backbone.<sup>61</sup>

### Light Emission

PS3DPA possesses two potential light-emitting species: one is the silole pendant, and the other is

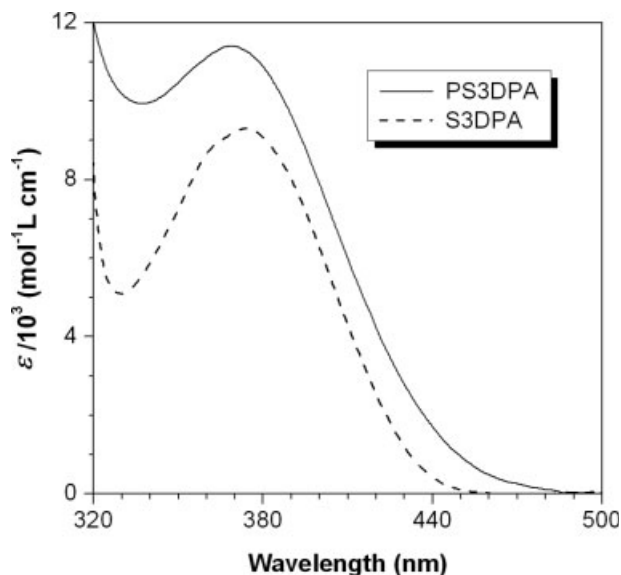


**Figure 3.**  $^{13}\text{C}$  NMR spectra of (A) S3DPA and (B) PS3DPA (sample from Table 1, no. 6) in  $\text{CD}_2\text{Cl}_2$  (the asterisk indicates the solvent peak).

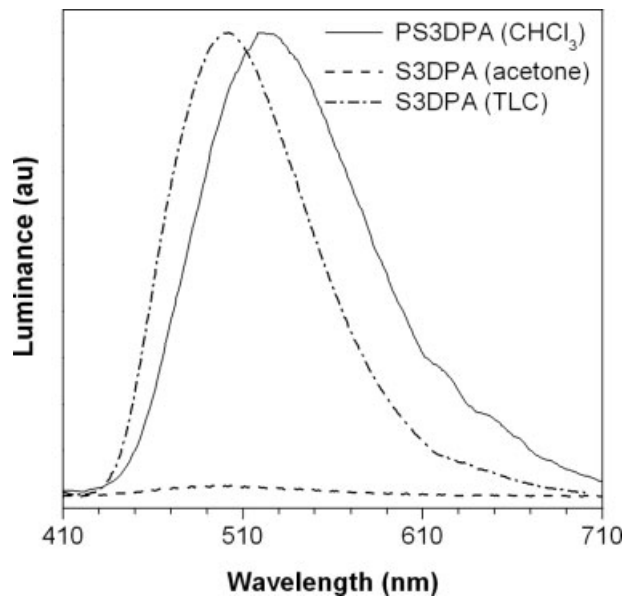


**Figure 4.** TGA and DSC thermograms of PS3DPA (sample from Table 1, no. 6) recorded under nitrogen with heating rates of 20 and 5 °C/min for the TGA and DSC measurements, respectively.

the polyene backbone. It would be interesting to determine how they dominate the light emission of the polymer. The PL spectra of PS3DPA in chloroform and S3DPA in acetone and on a thin-layer chromatography (TLC) plate are shown in Figure 6. The chloroform solution of PS3DPA emitted a green light of 523 nm, which was located in the emission range of PDPAs.<sup>59</sup> Thus, the PL of PS3DPA in the solution was a backbone-domi-



**Figure 5.** UV absorption spectra of chloroform solutions of PS3DPA (sample from Table 1, no. 6) and its monomer S3DPA.

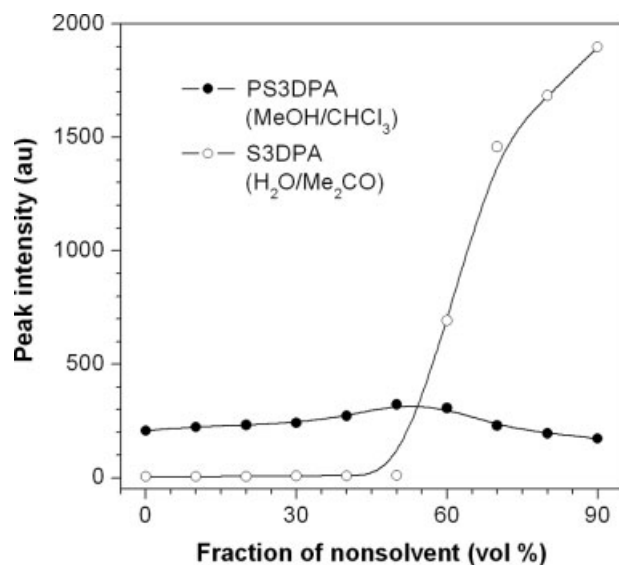


**Figure 6.** PL spectra of PS3DPA (Table 1, no. 6) in chloroform ( $1 \times 10^{-5}$  mol/L) and S3DPA in acetone ( $1 \times 10^{-5}$  mol/L) and on a TLC plate (excitation wavelength = 400 nm).

nated light emission. S3DPA was nearly nonluminescent in solution, and its  $\Phi_{\text{PL}}$  value in acetone was only  $\sim 0.06\%$  (estimated with 9,10-diphenylanthracene as the reference).<sup>3</sup> This is a general phenomenon for silole compounds in solutions. The S3DPA that adsorbed on a TLC plate displayed an intense blue-green light emission that peaked at 502 nm, which was identical to the PL peak of 1-ethynyl-1,2,3,4,5-pentaphenylsilole.<sup>3</sup> The  $\Phi_{\text{PL}}$  value of PS3DPA in chloroform was 2.8%, much higher than that of S3DPA in solutions. The  $\Phi_{\text{PL}}$  value of PS3DPA in the solution was about 14 times higher than those ( $\sim 0.2\%$ ) of PS9A and PS9PA in solutions.

Although silole molecules in a solution are almost nonluminescent, its aggregates formed by the addition of a large amount of a nonsolvent are highly emissive.<sup>3</sup> We checked the light emission of the aggregates of PS3DPA formed in solvent mixtures. No largely enhanced emission was, however, observed when up to 90 vol % methanol was added to its chloroform solution (Fig. 7). The behavior of S3DPA in a water/acetone mixtures is shown in the same figure for comparison. When water, a nonsolvent of S3DPA, was added to the acetone solution, a sharp increase in the PL intensity was observed at a water fraction higher than 50% because of the aggregation of S3DPA.<sup>3</sup> When the water fraction was increased to 90%, the PL peak intensity of the aggregates of S3DPA





**Figure 7.** Peak intensity of PL of PS3DPA (Table 1, no. 6) versus the solvent composition of a methanol/chloroform mixture (concentration of PS3DPA =  $1 \times 10^{-5}$  mol/L, excitation wavelength = 400 nm). The data for S3DPA in water/acetone mixtures are shown for comparison ( $1 \times 10^{-5}$  mol/L).

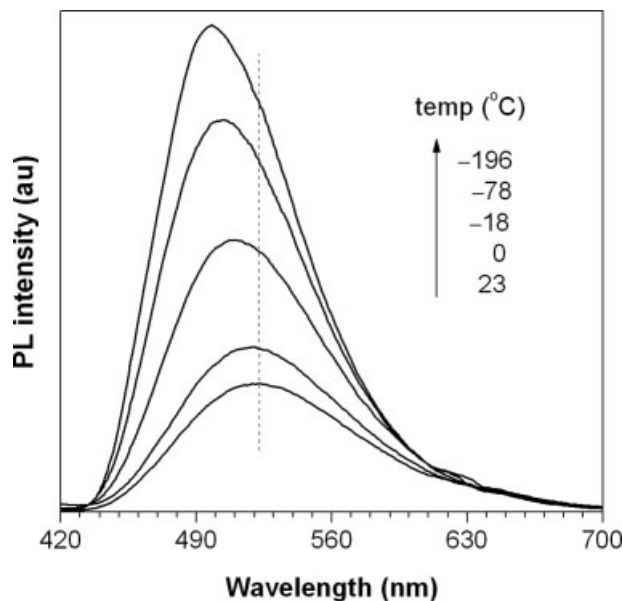
was 380 times higher than that of its acetone solution, revealing that S3DPA is AIE-active.

The AIE-inactive nature of PS3DPA might be due to the high rigidity of the PDPA backbone, which impedes the formation of the silole clusters in the polymer aggregates. According to the mechanism for the PL of siloles, intramolecular phenyl rotations provide a nonradiative pathway, whereas restriction of the intramolecular rotations populate the radiative decay.<sup>3</sup> Because of the difficulty in the congregation of the silole pendants in the polymer and the possibly large free volumes in PDPA chains,<sup>60</sup> the intramolecular phenyl rotations of the silole moieties may have been hardly restricted in the polymer aggregates.

Cooling is another way of restricting the intramolecular phenyl rotations, which gives rise to the CEE behavior of silole solutions.<sup>3</sup> We chose dioxane, a common solvent with a high melting point (mp = 11.8 °C) that solidifies with a small extent of cooling from room temperature. The PL spectra of PS3DPA in dioxane at different temperatures are shown in Figure 8. The PL intensity increased with decreasing temperature. At room temperature, the PL spectrum of the dioxane solution of PS3DPA peaked at 522 nm. Along with decreasing temperature, a blueshift in the PL spectrum was observed. At

−196 °C, the dioxane solid of PS3DPA emitted at 498 nm, close to the peak position (502 nm) of S3DPA in the solid state. The blueshift of the PL spectra should be attributed to the contribution by the gradually enhanced emission of the silole moiety along with the cooling process. The light emission at a low temperature should also contain the contribution from the polyene backbone. The reason that only one peak, instead of two peaks, was observed is probably the merger of the two emission bands. The light emission of the dioxane solid of PS3DPA at −196 °C should be regarded as a silole-dominant emission. The results also imply that the excitation energy transfer from the silole pendants to the polyene backbone is limited. The peak intensity of the PL spectrum changed with temperature in a nonlinear fashion in dioxane (Fig. 9).

To separate the cooling effect from the glass effect, we chose THF, a liquid with a high solvation power but a low melting point (mp = −105 °C), which could keep both the solvent and the solute in the solution state during the cooling process. From room temperature to −78 °C, the peak intensity of the PL spectrum of a dilute THF solution of PS3DPA ( $1 \times 10^{-5}$  mol/L) was weaker than that of the dioxane solution or glass (Fig. 9) because of the stronger solvating power of THF to the polymer. The PL intensity in-

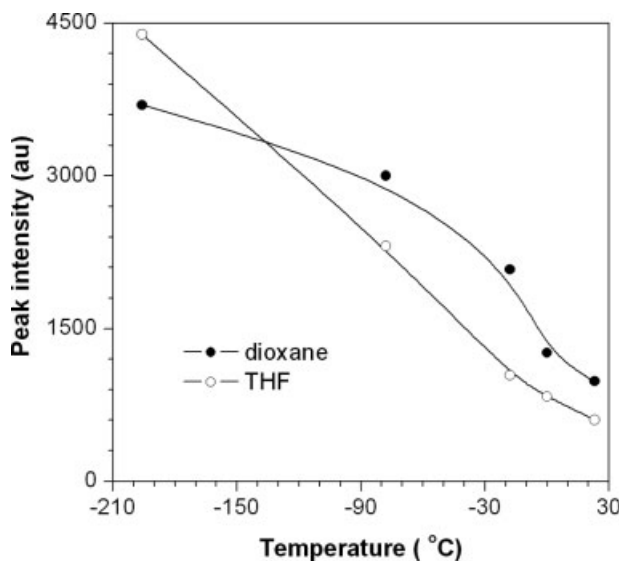


**Figure 8.** PL spectra of PS3DPA (sample from Table 1, no. 6) in dioxane at different temperatures (concentration of PS3DPA =  $1 \times 10^{-5}$  mol/L, excitation wavelength = 407 nm).

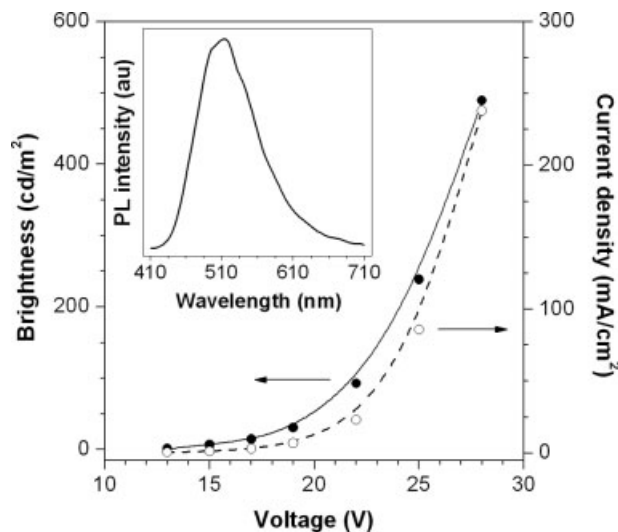
creased with a decrease in temperature in a nearly linear fashion. At  $-78\text{ }^{\circ}\text{C}$ , the solution was transparent; thus, the solvent should have been in the liquid state and the solute should have been molecularly dissolved from room temperature to  $-78\text{ }^{\circ}\text{C}$ . Therefore, the enhanced emission must have been due to the stronger restriction to intramolecular phenyl rotations resulting from the cooling effect. With further cooling to  $-196\text{ }^{\circ}\text{C}$ , THF was also frozen. The PL intensity was greatly increased, higher than that of the dioxane glass.

Light-emitting conjugated polymers are promising candidate materials for applications in the construction of flat-panel displays.<sup>62–64</sup> We fabricated an EL device of PS3DPA with a configuration of ITO/(1:4 PS3DPA/PVK)/BCP/Alq<sub>3</sub>/LiF/Al. As shown in Figure 10, a green light emission that peaked at 512 nm was observed from the EL device. The peak position was between the pendant and backbone emissions, possibly because of the contributions from the two emitting species.

The brightness–voltage–current density characteristics of the device are also shown in Figure 10. The device had a turn-on voltage of 13 V. Both the brightness and current density increased with the voltage exponentially. At a bias of 28 V or a current density of 238 mA/cm<sup>2</sup>, the maximum brightness of the device reached 489 cd/m<sup>2</sup>. The maximum current efficiency and external quantum efficiency of the device were 0.53 cd/A and 0.19%, respectively, at a voltage of 15 V.



**Figure 9.** Effect of temperature on the peak intensity of the luminescence of PS3DPA (Table 1, no. 6) in dioxane and THF (concentration of PS3DPA =  $1 \times 10^{-5}$  mol/L, excitation wavelength = 407 nm).



**Figure 10.** Brightness–voltage–current density characteristics of an EL device of PS3DPA with a device configuration of ITO/(1:4 PS3DPA/PVK)/BCP/Alq<sub>3</sub>/LiF/Al. The inset shows the EL spectrum of the device.

## CONCLUSIONS

In this work, a new PDPA derivative with a silole pendant has been synthesized and characterized. Only the ethynyl group of the diphenylacetylene moiety is polymerized, whereas the ethynyl group connecting the silolyl group does not change during the polymerization. Upon photoexcitation, the polymer solution at room temperature emits a green light because of the PDPA backbone emission. The polymer is AIE-inactive because of the very high rigidity of the PDPA main chain, which impedes the formation of silole clusters during the formation of polymer aggregates. Because the agglomeration of PDPA chains generates large free volumes, the peripheral phenyl rings attached to the silole pendants may still have the freedom to undergo intramolecular rotations. The intramolecular rotations can be readily restricted by cooling. The polymer solutions exhibit CEE with a continuous blue-shift because of the increasing contribution from the silole emission, finally ending with a silole-dominant emission at the lowest temperature. This also implies that the excitation energy transfer from the silole pendants to the PDPA backbone is limited at the cryogenic temperature. A multilayer EL device of the polymer emitted a green light with a maximum brightness of 489 cd/m<sup>2</sup>. The maximum current efficiency and the external quantum efficiency were 0.53 cd/A and 0.19%, respectively.

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