

## LINEAR AND HYPERBRANCHED POLYMERS WITH HIGH THERMAL STABILITY AND LUMINESCENCE EFFICIENCY

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**Abstract** New acetylene monomers, 6-[[1-(naphthylethynyl-4-phenyl)carbonyl]oxy]-1-phenyl-1-hexyne (**1**), 2,5-diethynylthiophene (**3**), and 4,4'-diethynylbiphenyl (**6**) were synthesized. Homopolymerization of **1** and copolycyclotrimerizations of **3** and **6** with 1-heptyne and 1-octyne have been achieved with  $\text{WCl}_6$ - and  $\text{TaCl}_5$ - $\text{Ph}_4\text{Sn}$  catalysts, respectively, giving soluble linear disubstituted polyacetylene (**2**) and hyperbranched polyarylenes (**5** and **8**) with high molecular weights (up to  $1.2 \times 10^5$ ) in high yields (up to 98%). The structures and properties of the polymers are characterized and evaluated by IR, NMR, TGA, UV, photoluminescence (PL), and electroluminescence (EL) analyses. All the polymers possess high thermal stability and emit strong blue light upon photoexcitation. The intensity of the emitted light is greater than that of poly(1-phenyl-1-octyne), a well-known highly luminescent disubstituted polyacetylene. Little aggregation-induced red shift in the PL was observed in the thin films of the polymers. By constructing a multi-layer EL device, high EL quantum yield (0.18%) has been achieved in **2**, which are the best results for substituted polyacetylenes attainable so far.

**Keywords** Disubstituted polyacetylene, Hyperbranched polyarylene, Light emission

## INTRODUCTION

Synthesis of blue-light emitting polymers has been the subject of intense academic and industrial research directed toward the fabrication of full color organic displays<sup>[1]</sup>. Poly(*p*-phenylene) (PPP), a thermally robust conjugated polymer, has attracted much attention as a promising candidate material for use in the construction of blue-light emitting diodes (LEDs)<sup>[2]</sup>. Its comparatively low solubility in organic solvents, however, precludes the formation of high molecular weight polymer. Different strategies have been developed to improve the processibility of PPP and its cousins such as polyfluorene have been prepared. The solubility of the polymers is, however, still a thorny problem restricting their potential applications as advanced materials.

Our group has recently launched a research program on the synthesis of luminescent polymers via transition metal-catalyzed (co)polymerizations of acetylene monomers. Through systematic investigations, we succeeded in developing catalytic systems for the preparations of disubstituted polyacetylenes bearing light-emitting pendants and hyperbranched polyarylenes of different architectures<sup>[3-9]</sup>. The properties of the resulting polymers are characterized by standard spectroscopic methods and most of them display strong photoluminescence (PL), good solubility, and excellent thermal stability. These promising results have motivated us to pursue polymers with long-term stability, high efficiency, and bright blue emission for commercially viable LEDs.

In this paper, we present the unique electrooptical properties of a novel disubstituted polymer bearing naphthylethynylphenyl moiety (**2**) and hyperbranched polyarylenes (**5** and **8**) containing thiophene and biphenyl

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## EXPERIMENTAL

Tungsten(VI) chloride, tantalum(V) chloride, tetraphenyltin, and tri(8-quinolinolato)aluminium (Alq<sub>3</sub>) were purchased from Aldrich and used without further purification. Acetylene monomers, 6-[[[1-naphthylethynyl-4-phenyl]carbonyl]oxy]-1-phenyl-1-hexyne (**1**), 2,5-diethynylthiophene (**3**) and 4,4'-diethynylbiphenyl (**6**) were prepared following the procedures described previously<sup>[10–12]</sup>. 1-Heptyne (**4**) and 1-octyne (**7**) were purchased from Aldrich and distilled over calcium hydride prior to use.

All the polymerization reactions and manipulations were carried out under nitrogen using an inert-atmosphere glovebox (Vacuum Atmosphere), except for the purification of the polymers, which was done in an open atmosphere.

The polymerization of **1** was achieved by  $\text{WCl}_6\text{-Ph}_4\text{Sn}$ /toluene complex at 60 °C for 24 h. Detailed procedures can be found in our previous paper<sup>[13]</sup>. Pale green powdery solid; yield 37.9%.  $M_w = 21850$ ,  $M_w/M_n = 2.4$ .  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 6.9–8.3 (br, Ar–H), 3.8 (br,  $\text{CO}_2\text{CH}_2$ ) and 2.5–2.3 [br,  $(\text{CH}_2)_3$ ].

Copolycyclootrimerization of diynes and monodynes were initiated by  $\text{TaCl}_5\text{-Ph}_4\text{Sn}$  catalyst in toluene at room temperature. A typical experimental procedures for the copolycyclootrimerization of **3** with **4** is given below. In a thoroughly baked and moisture excluded Schlenk tube was placed 18.0 mg of  $\text{TaCl}_5$  (0.05 mmol) and 12.3 mg of  $\text{Ph}_4\text{Sn}$  (0.05 mmol) in a glovebox. The catalysts were mixed with 1.0 mL toluene and aged at room temperature for 15 min. A solution of 33 mg (0.25 mmol) **3** and 30  $\mu\text{L}$  (0.225 mmol) **4** in 1.45 mL toluene was

then added dropwise to the catalyst solution. After stirring at room temperature for 20 h, the reaction was quenched by the addition of a small amount of menthol. The polymer solution was dropped into 300 mL menthol via a cotton filter under stirring to precipitate the polymer. The crude product was further purified by pouring its chloroform solution into hexane. A brown powder (**5**) was collected and dried in vacuum overnight. Yield 65.5%.  $M_w = 33500$ ,  $M_w/M_n = 8.1$ .  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 6.5–8.0 (br, Ar-H), 2.6 (s, Ar- $\text{CH}_2$ ) and 0.6–1.8 [br,  $(\text{CH}_2)_3\text{CH}_3$ ].

The procedure for copolycyclotrimerization of **6** with **7** is similar to the above except that the molar ratio between diyne and monoyne is 1:1.19. Yield 97.8%.  $M_w = 116800$ ,  $M_w/M_n = 3.3$ .  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.0–8.0 (br, Ar-H), 2.5 (s, Ar- $\text{CH}_2$ ) and 0.5–2.0 [br,  $(\text{CH}_2)_4\text{CH}_3$ ].

### Instrumentation

$^1\text{H-NMR}$  spectra were recorded on a Bruker ARX 300 spectrometer using dichloromethane- $d_2$  as solvent and tetramethylsilane (TMS) as internal reference. The thermal stability of the polymers was evaluated on a Perkin-Elmer TGA 7 at a heating rate of 20 K/min under nitrogen. Fluorescence spectra of the polymers were recorded on a SLM spectrofluorometer. PL and electroluminescence (EL) spectra of the polymer thin films were obtained on a Kollmorgen Instrument PR650 photospectrometer. The luminescence area was 12.6 mm<sup>2</sup>. Current-voltage ( $I$ - $V$ ) characteristics were obtained using a Hewlett-Packard HP4145B Semiconductor Analyzer.

### EL Device Construction

The cell configuration is shown in Chart 1. The sheet resistance of ITO coated glass substrate is 10–20  $\Omega$ /square. The polymer thin film was prepared by spin coating from its toluene solution (5 mg/mL). The thickness of the polymer thin film was between 35 and 60 nm. The bathocuproine (20 nm),  $\text{Alq}_3$  [electron-transporting layer (ETL); 30 nm], LiF [electron-injection layer (EIL); 0.8 nm] and Al (150 nm) layers were deposited in turn under vacuum ( $2 \times 10^{-6}$  Torr).

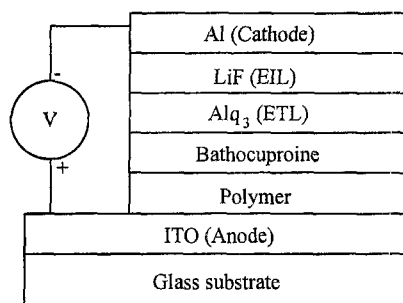


Chart 1

## RESULTS AND DISCUSSION

With a view to synthesizing polymers with novel electrooptical properties, we prepared a phenylalkyne derivative bearing a naphthylethynylphenyl moiety (**1**) and two diacetylenes (**3** and **5**) by multi-step reactions. All the reactions proceeded smoothly and the products were isolated in high yields. The monomers were characterized by standard spectroscopic methods and satisfactory analysis data were obtained.

Polymerization of **1** was initiated by  $\text{WCl}_6\text{-Ph}_4\text{Sn}$  catalyst in toluene at 60°C, yielding 38% of pale green powdery product by precipitation of its toluene solution into acetone. The resulting polymer is highly soluble in organic solvents, suggesting that  $\text{WCl}_6\text{-Ph}_4\text{Sn}$  catalyst selectively polymerizes the 1-phenyl-1-hexyne structure without generating any crosslinking side products.

Unlike the situation in **1**, homopolycyclotrimerizations of **3** and **6** by  $\text{TaCl}_5\text{-Ph}_4\text{Sn}$  in toluene at room temperature give insoluble gels. To suppress crosslinking and improve the solubility of the resulting polyarylenes, copolymerizations of the diacetylenes with monodynes are carried out. Both **3** and **6** copolymerize

well with **4** and **7** and soluble; high molecular weight polymers (up to  $1.2 \times 10^5$ ) were obtained in high yields (up to 98%).

All the polymers give satisfactory analysis data corresponding to their expected molecular structures. Figure 1(a) shows the  $^1\text{H}$ -NMR spectrum of **5**. The absorptions of the acetylene protons in **3** and **4** at  $\delta = 1.9$  and 3.5 disappear after polymerization. The peaks of the aromatic protons broaden significantly from  $\delta = 6.8$  to 8.0, confirming the high selectivity of the copolycyclotrimerization reaction and the proposed structure given in Scheme 1. The spectrum also provides information on the degree of branching (DB) for the polymer. Using Fréchet formula<sup>[14]</sup>, the DB for **5** is evaluated to be not lower than 0.24, revealing that hyperbranched, instead of linear, poly[phenylene-*alt*-(2,5-thienylene)] is obtained. The spectral pattern of **8** is similar to that of **5**.

TGA thermograms of the polymers are given in Fig. 1(b). Polymer **2** possesses high thermal stability and its onset temperature is up to  $\approx 350^\circ\text{C}$ . Much higher resistance to thermolysis was observed for **5** and **8**, and the high thermal stability further verifies the proposed hyperbranched structure.

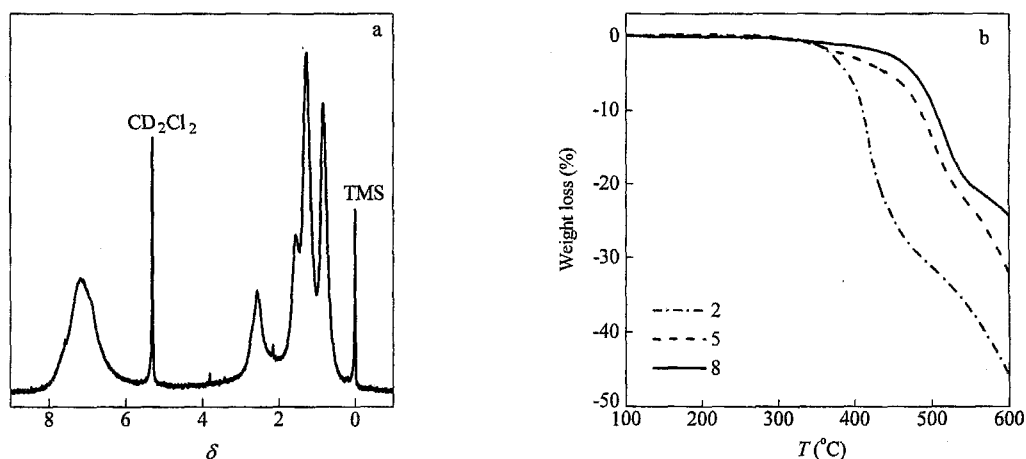


Fig. 1 (a)  $^1\text{H}$ -NMR spectrum of **5** in  $\text{CD}_2\text{Cl}_2$ ; (b) TGA thermograms of **2**, **5** and **8** recorded under nitrogen at a heating rate of 20 K/min

After confirming the thermal stability of the polymers, we investigated their electrooptical properties. When **2** is irradiated at 362 nm, it emits blue light of 470 nm (Fig. 2a), whose intensity is 5 times higher than that of poly(1-phenyl-1-octyne) (PPO), a well-known highly luminescent disubstituted polyacetylene. Most conventional linear polymers such as PPP show less efficient emissions at longer wavelengths owing to its strong interchain  $\pi$ -stacking in the solid states<sup>[15]</sup>. However, we observed intense blue-light emission when a thin film of **2** was excited at 325 nm. Moreover, little shift in peak maximum was found when compared to that in solution. This unusual behavior may be attributed to the bulky pendant, which strongly reduces the interaction between the polymer chains.

The efficiency of a single layer EL cell is usually low owing to imbalanced injection of electrons and holes. One effective method to increase the EL efficiency is to insert an electron-transporting layer between the emissive layer and the metal cathode.  $\text{Alq}_3$  is a good electron-transporting material but its strong EL always suppresses the light emitted by the polymer. Thus, to prevent interference from  $\text{Alq}_3$ , a hole-blocking layer (bathocuproine) is usually applied above the polymer layer<sup>[16]</sup>. By constructing multi-layer device as shown in Chart 1, the EL of **2** was observed at 488 nm. The EL spectrum is nearly identical to the PL spectrum, suggesting that they all originate from the radiative decay of the singlet excitons induced by the photoexcitation or the charge recombination. Figure 2(b) shows the changes of the EL and current intensities with the applied bias. The turn-on voltage is 8 V but the light is too low for detection until the bias rises to 11 V. Afterwards, the EL intensity increases and reaches a maximum at 12 V ( $3.3 \text{ cd/cm}^2$ ). The corresponding EL current efficiency and quantum yield at this voltage are 0.20 cd/A and 0.18%, which are five times higher than those of poly[1-(*p*-*n*-

butylphenyl)-2-phenylacetylene) doped with 2-(4-biphenyl)-5-(4-*t*-butylphenyl)-1,3,4-oxadiazole, a charge-transporting material<sup>[17]</sup>. The EL intensity drops when the voltage exceeds 13 V. On the other hand, the current density flowing through the device is proportional to the applied bias.

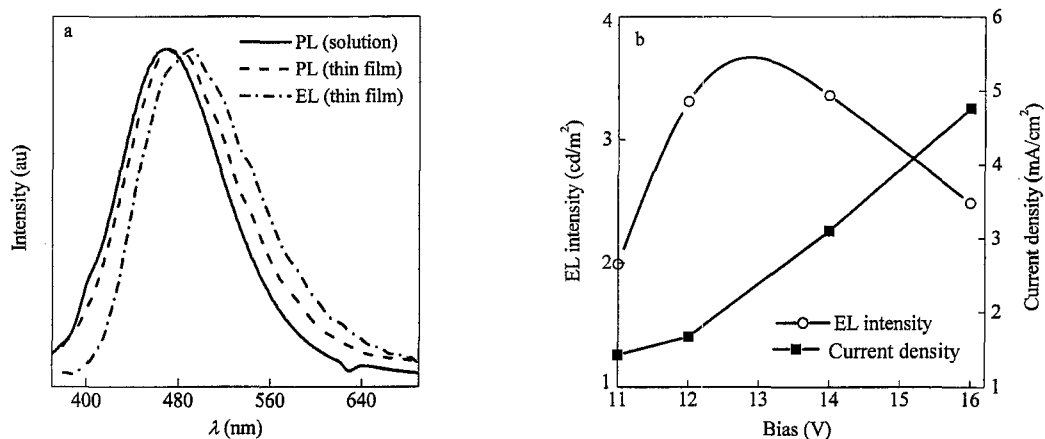


**Fig. 2** (a) PL and EL spectra of THF solution and thin film of **2**; (b) Changes of the EL and current intensities with the applied bias

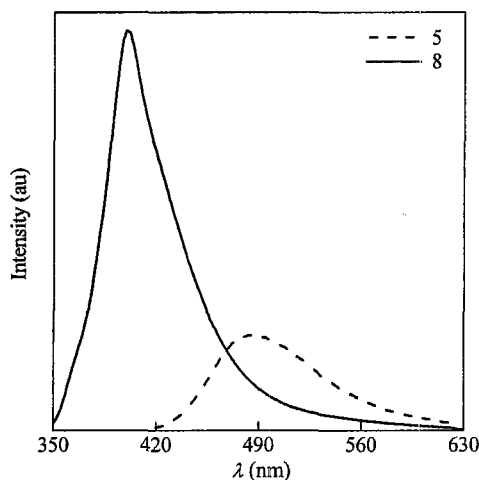


**Fig. 3** Fluorescence spectra of dichloromethane solutions of **5** and **8**

The fluorescence spectra of **5** and **8** are shown in Fig. 3. Upon UV irradiation at 410 nm, strong PL, similar to that of PPO, was emitted from **5** at 486 nm. Much higher luminescence was observed at 400 nm when the dichloromethane solution of **8** was excited at 342 nm. The excellent fluorescence of the copolymers seems to arise from their unique structure containing the thiophene and biphenyl chromophores. We also investigated the PL of thin films of the copolymers and found that the emission maxima are slightly bathochromically shifted. This minor shift is a sign of little aggregation in the solid states of **5** and **8**. Undoubtedly, the dendritic units of the copolymers provide a nanoenvironment for effective site isolation. EL of the copolymers is currently under investigation in our laboratories.

## CONCLUSION

Soluble disubstituted polyacetylene bearing a naphthylethynylphenyl moiety (**2**) and hyperbranched polyarylenes containing thiophene and biphenyl chromophores (**5** and **8**) have been prepared. The structures of the polymers

are thoroughly characterized by common spectroscopic methods. All the polymers possess good thermal stability, and strong blue emissions are observed upon photoexcitation, whose intensities are higher than that of PPO. Experimental results show that the tendency of aggregate formation in the thin solid films of the polymers is significantly suppressed. By constructing a multi-layer EL device, high EL quantum yield (0.18%) has been achieved in **2**. We recently found that the polyarylenes display novel optical limiting behavior<sup>[11, 12]</sup>. Thus, these polymers can be considered as speciality materials with multifunctional properties.

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