

## Synthesis and Properties of Oligomers Containing 1,4-Bis(thiophene)buta-1,3-diyne and Bisphenol-A Derivatives

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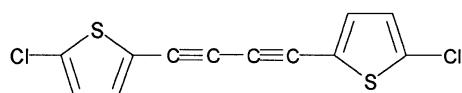
Conjugated polymers containing organic conjugate groups such as thiophene and acetylene have received considerable attention for the potential applications of electronic and optical materials in recent years.<sup>1-3</sup> We have recently prepared a new monomeric compound of 1,4-bis(5-chlorothiophenyl)buta-1,3-diyne, which contains organic conjugate groups such as both thiophene and diacetylene simultaneously.<sup>4</sup> We have also reported the synthesis and properties of novel polycarbosilanes as well as polycarbogermenes containing 1,4-bis(thiophene)buta-1,3-diyne in the polymer main chain,<sup>4,5</sup> and their excited-state energy dynamics.<sup>6</sup> The polycarbosilanes and polycarbogermenes were prepared by the treatment of 1,4-bis(5-chlorothiophenyl)buta-1,3-diyne with *n*-butyllithium followed by co-polymerizations with dichlorodioro-organosilanes and dichlorodioro-germanes, respectively.

We have also been interested in an aromatic nucleophilic substitution polymerization of 1,4-bis(5-chlorothiophenyl)buta-1,3-diyne. Herein we describe the synthesis of new oligomeric materials containing 1,4-bis(thiophene)buta-1,3-diyne and bisphenol-A derivatives in their main chains by nucleophilic substitution reaction along with the electronic and thermal properties of the obtained oligomers.

### Results and Discussion

**Synthesis of Oligomers.** The monomer, 1,4-bis(5-chlorothiophenyl)buta-1,3-diyne (**1**) was prepared in a three-step procedure from commercially available 2-bromo-5-chlorothiophene according to the previously reported method (Scheme 1).<sup>4</sup>

The synthetic route for oligomers containing 1,4-bis(thiophene)buta-1,3-diyne and bisphenol-A derivatives is outlined in Scheme 2. The copolymerization between **1** and bisphenol-A (**2**) was carried out in *N*-methyl-2-pyrrolidone (NMP)/toluene as solvent mixture in the presence of K<sub>2</sub>CO<sub>3</sub>

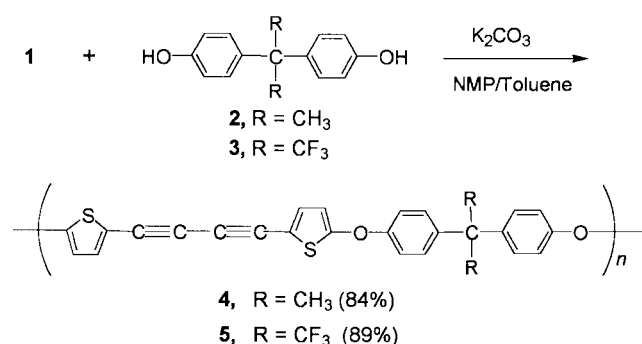


Scheme 1

by a nucleophilic substitution reaction<sup>7,8</sup> to afford the oligomer of poly[(1,4-bis(thiophene)buta-1,3-diyne)-*co*-(bisphenol-A)] (**4**). Toluene was used to remove the water generated upon heating to 110 °C by azeotrope using a Dean-Stark trap. The material **4** was obtained in high yield as a black powder in the type of oligomer with a number-average molecular weight ( $M_n$ ) of  $1.42 \times 10^3$  and a polydispersity ( $M_w/M_n$ ) of 1.80. The oligomer of poly[(1,4-bis(thiophene)buta-1,3-diyne)-*co*-(hexafluorobisphenol-A)] (**5**) was also prepared in high yield following the same procedure for **4** using hexafluorobisphenol-A (**3**) as comonomer. The obtained material **5** was found to be a black powder in the form of oligomer with  $M_n$  of  $1.44 \times 10^3$  and a polydispersity of 1.97.

The obtained oligomeric materials have also been characterized by <sup>1</sup>H NMR, IR spectra, as well as elemental analyses. The selected spectral data of oligomers **4** and **5** are summarized in Table 1. In particular, the characteristic C≡C stretching frequencies are observed at 2300 cm<sup>-1</sup> in the IR spectra of **4** and **5**, indicating that the diacetylene groups remain intact during polymerization reactions.<sup>9</sup> The elemental analyses data, which were included in the Experimental Section, were in good agreement with the proposed structure.

**Properties of Oligomers.** The oligomers **4** and **5** were soluble in common organic solvents such as THF and chloroform. The solubility of all the oligomers **4** and **5** allows us to perform studies on the properties in solution. The UV-vis absorption and the excitation spectra of **4** and **5** in THF were shown in Figures 1 and 2, respectively. The strong absorption bands with broad and weak tailing are observed in the absorption spectra of **4** and **5** (see the inset



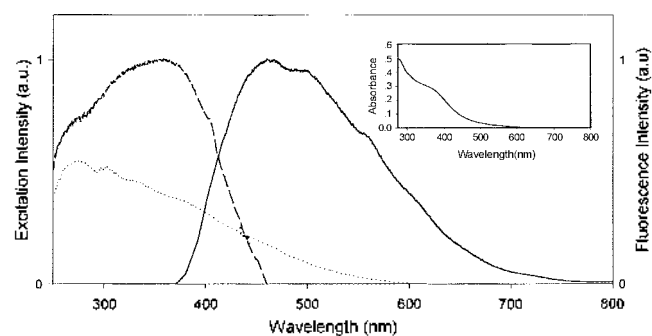
Scheme 2

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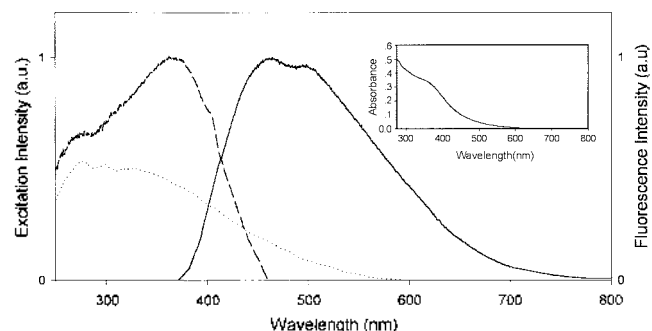
**Table 1.** Selected Properties of the Oligomers **4** and **5**

Oligomer	$M_n^a$	$M_w/M_n^a$	$^1\text{H NMR}$ $\delta$ (ppm)	IR $\nu_{(\text{C}=\text{C})}$ ( $\text{cm}^{-1}$ )	Fluorescence $^{b,c}$ $\lambda_{\text{max}}$ (nm)	TGA $^d$
<b>4</b>	$1.42 \times 10^3$	1.80	1.40-1.60 (bs), 6.50-7.60 (m)	2300	460	76
<b>5</b>	$1.44 \times 10^3$	1.97	6.60-7.60 (m)	2300	465	84

<sup>a</sup>Determined by GPC in THF relative to polystyrene standards. <sup>b</sup>In THF. <sup>c</sup>Excitation wavelength of 360 nm. <sup>d</sup>% Weight remaining at 400 °C in nitrogen.



**Figure 1.** Fluorescence spectrum at 360 nm excitation (solid), excitation spectra at 460 nm of detection (short dash), and at 600 nm of detection (dotted) of **4** in THF. Inset is the absorption spectrum of **4** in THF.



**Figure 2.** Fluorescence spectrum at 360 nm excitation (solid), excitation spectra at 460 nm of detection (short dash), and at 600 nm of detection (dotted) of **5** in THF. Inset is the absorption spectrum of **5** in THF.

spectra in Figures 1 and 2, respectively). The excitation spectra for **4** and **5** at the detection wavelength of 460 nm show the strong excitation bands at the  $\lambda_{\text{max}}$  of 361 and 371 nm, respectively. The broad and weak excitation bands are also observed at the detection wavelength of 600 nm for both **4** and **5**. These strong absorption and excitation bands may be attributed to the chromophores such as thiophene, diacetylene, bisphenol-A derivatives, and partially delocalized  $\pi$ -conjugate groups along the backbone. The time-resolved spectroscopic experiments are being in progress to understand the origins of these excitation bands.

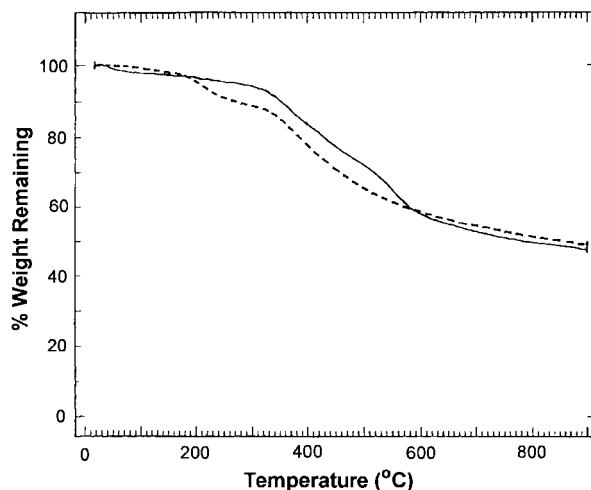
The fluorescence emission spectra of **4** and **5** at the excitation wavelength of 360 nm in THF were also shown in Figures 1 and 2, respectively. The fluorescence spectra of **4** and **5** indicate the strong emission peaks at the  $\lambda_{\text{max}}$  of 460 nm with the emission band of 374-760 nm and at the  $\lambda_{\text{max}}$  of 465 nm with the emission band of 375-760 nm, respectively.

These strong emission peaks are due to the fluorophores of  $\pi$ -conjugated system in the oligomers **4** and **5**, which contain the partially delocalized  $\pi$ -conjugate group along the main chain.

Although the origins of such broad fluorescence spectra are not clear at this moment, the observed broadness of the emission spectra includes an important application respect in electro-optic field as the white light continuum generation that is not usual property especially for the low molecular weight oligomers. Such phenomenon usually depends on the several factors which can be the inhomogenities in the number of repeating units of the prepared oligomers, the electronic energy dynamics of  $\pi$ -conjugation along the backbone, and the geometrical molecular structures in their electronic ground and/or excited states. The time resolved fluorescence spectroscopic studies on these factors are also in progress.

The thermal stabilities of oligomers **4** and **5** in nitrogen atmosphere were determined by thermogravimetric analysis (TGA). Oligomer **4** is thermally stable up to 150 °C. Rapid weight loss of 33% occurs between 260 and 650 °C. When **4** is heated to 900 °C by the heating rate of 10 °C/min, a residue of 50% remains (see the broken line in Figure 3). Oligomer **5** is thermally stable to 200 °C. Rapid weight loss of 36% occurs between 300 and 600 °C. At 900 °C, 48% of the initial sample weight of **5** remains (see the solid line in Figure 3).

On the differential scanning calorimetry (DSC) curves of the obtained oligomers, the anticipated exothermic peaks due to the cross-linking of diacetylene group were not observed, while the exothermic ones were reported in the



**Figure 3.** TGA thermograms of **4** (----) and **5** (—) in nitrogen.

diacetylene-containing organic polymers such as poly(2,5-diethynylthiophene)<sup>10</sup> as well as the copolymer of 1,4-bis(4-fluorophenyl)buta-1,3-diyne and hexafluorobisphenol-A.<sup>7</sup>

In conclusion, we have successively prepared the oligomeric materials which contain 1,4-bis(thiophene)buta-1,3-diyne and bisphenol-A derivatives in the main chain. All of these materials are soluble in THF as well as chloroform, and are thermally stable up to 150 °C under nitrogen. The UV-vis absorption and the excitation spectra exhibit the strong absorption bands with broad and weak tailing. The fluorescence spectra show the broad emission bands of 374-760 nm with the emission  $\lambda_{\text{max}}$  values in the range of 460-465 nm. Both the strong absorption and emission spectra indicate that the obtained oligomers contain the conjugate groups such as thiophene, diacetylene, and bisphenol-A derivatives as well as partially delocalized  $\pi$ -conjugate groups in the their main chain. Furthermore, both the strong absorption and emission spectra suggest the application possibility of these molecular systems as strong white light emission mediums.

### Experimental Section

**General Procedures.** All chemicals were purchased from Aldrich Chemicals Co. Solvents were purified by conventional methods and were freshly distilled under argon prior to use. All reactions were carried out under argon atmosphere. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on either a Bruker ARX 300 or a JEOL JNM-EX90A spectrometer. Chemical shifts were measured using tetramethylsilane or the solvent as internal standards. IR spectra were recorded with either a Bruker IFS-48 or a Shimadzu IR-470 spectrometer. UV-vis spectra were run on a Hewlett Packard 8452A spectrophotometer. Fluorescence emission spectra were obtained on a Hitachi F-4500. Gel permeation chromatography (GPC) analyses were performed on a Waters model 510 system with a Waters Styragel HR 3 column and refractive index detector at 25 °C. The eluent was THF at a flow rate of 1.0 mL/min. The calibration was made with a series of monodispersed polystyrene standards. Thermogravimetric analyses (TGA) were performed on a Shimadzu TGA-50 instrument. The temperature was increased at the rate of 10 °C/min from 25 to 900 °C with nitrogen flow rate of 20 mL/min.  $T_g$  was measured by differential scanning calorimetry in nitrogen on a Perkin-Elmer DSC-7. Elemental analyses were performed by a Fisons EA 1108 elemental analyzer.

**1,4-Bis(5-chlorothiophenyl)buta-1,3-diyne (1)** was prepared from 2-bromo-5-chlorothiophene according to the previously reported method.<sup>4</sup>

**Copolymerization of Monomer 1 and Bisphenol-A (2).** In a 250 mL three-necked round bottom flask equipped with an argon inlet, stirring bar, Dean-Stark trap, and condenser, **1** (1.50 g, 5.3 mmol), **2** (1.21 g, 5.30 mmol) and NMP (60 mL) were placed under argon atmosphere. K<sub>2</sub>CO<sub>3</sub> (1.10 g, 7.95 mmol) and 40 mL of toluene were then added. The reaction mixture was heated until the toluene began to reflux. Water

formed during the reaction was removed as an azeotrope with toluene over 4-5 h periods. The reaction mixture was slowly raised to 180-190 °C for 2-3 h. The polymer was isolated by precipitating into 100 mL of methanol, and washed with water/methanol 4-5 times to remove excess salts. The suspension was warmed with water/methanol, filtered, and dried in a vacuum oven at room temperature. Poly[(1,4-bis(thiophene)buta-1,3-diyne)-*co*-(bisphenol-A)] (**4**), 1.91 g, 84% was obtained as a black powder with 2.560/1.420 ( $M_w/M_n$ ). <sup>1</sup>H-NMR (THF-*d*<sub>8</sub>, 90MHz):  $\delta$  1.40-1.60 (bs, 6H), 6.50-7.60 (m, 12H); IR (KBr pallet):  $\nu$  3350, 3100, 2960, 2300, 1660, 1600, 1500, 1410, 1380, 1360, 1215, 1170, 1050, 830, 700 cm<sup>-1</sup>; Anal. Calcd for (C<sub>27</sub>H<sub>18</sub>O<sub>2</sub>S<sub>2</sub>)<sub>n</sub>: C, 73.94; H, 4.14; S, 14.62. Found: C, 71.88; H, 4.22; S, 14.99. UV-vis absorption, excitation, and fluorescence spectra of **4** were measured in diluted THF solution ( $\cong 1.0 \times 10^{-6}$  M) and described in the Results and Discussion, as well as TGA thermogram.

**Copolymerization of Monomer 1 and Hexafluorobisphenol-A (3)** was carried out following the identical manner used in the preparation of **4**, using **1** (1.50 g, 5.30 mmol) and **3** (1.78 g, 5.30 mmol). Poly[(1,4-bis(thiophene)buta-1,3-diyne)-*co*-(hexafluorobisphenol-A)] (**5**), 2.56 g, 88% was obtained as a black powder with 2.830/1.440 ( $M_w/M_n$ ). <sup>1</sup>H-NMR (THF-*d*<sub>8</sub>, 90 MHz):  $\delta$  6.60-7.60 (m, 12H); IR (KBr pallet):  $\nu$  3350, 3100, 2960, 2300, 1700, 1660, 1605, 1505, 1435, 1370, 1260, 1240, 1170, 1130, 960, 830, 700 cm<sup>-1</sup>; Anal. Calcd for (C<sub>27</sub>H<sub>12</sub>F<sub>6</sub>O<sub>2</sub>S<sub>2</sub>)<sub>n</sub>: C, 59.34; H, 2.21; S, 11.73. Found: C, 59.46; H, 2.34; S, 11.14. UV-vis absorption, excitation, and fluorescence spectra of **5** were measured in diluted THF solution ( $\cong 1.0 \times 10^{-6}$  M) and described in the Results and Discussion along with TGA thermogram.

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