

Synthesis and Properties of Polycarbogermanes Containing 1,4-Bis(thiophene or phenylene)buta-1,3-diyne

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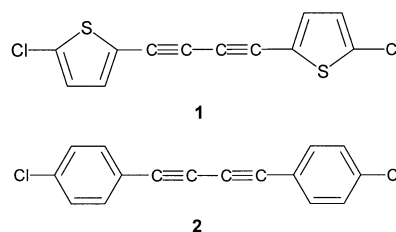
Conjugated polymers have received considerable attention for the potential applications of electrical and optical materials in recent years.¹ Poly[(silylene)diethynylenes] doped with ferric chloride show slightly higher values of electrical conductivity than those of the corresponding poly[(germylene)diethynylenes] under the same conditions.²⁻⁵ The conductivities of all silicon- and germanium-containing polymers treated with strong oxidizing agents are the level of semiconductors. Meanwhile, experimental and theoretical investigations on polycarbosilanes containing disilanylene unit and carbon π -conjugated moieties in their main chain have revealed σ/π conjugation phenomena along the polycarbosilanes backbone.^{6,7} Silicon-containing poly(*p*-phenylenevinylene) and poly(cyanoterephthalylidene) copolymers showed tunable electroluminescence for the possible application to blue light-emitting diodes.^{8,9} Polymers composed of regularly alternating organosilicon and conjugated carbon groups have been reviewed.¹⁰ However, little interest has been shown in the polycarbogermanes.

Recently, we have reported the synthesis and properties of new conjugated polycarbosilanes with 1,4-bis(thiophene or phenylene)buta-1,3-diyne along the polymer main chain,¹¹ as well as excited-state dynamics of the polymers.¹² Thus, as an extension to our previous work, we now report the synthesis of new polycarbogermanes containing 1,4-bis(thiophene or phenylene)buta-1,3-diyne along the polymer main chain and the electronic and thermal properties of the polymers.

Results and Discussion

Monomer and Polymer Synthesis. The monomers of 1,4-bis(5-chlorothiophenyl)buta-1,3-diyne (**1**) and 1,4-bis(5-chlorophenyl)buta-1,3-diyne (**2**) were prepared in three steps from commercially available 2-bromo-5-chlorothiophene and bromochlorobenzene, respectively, according to the previously reported method (Scheme 1).¹¹

The synthetic route for the polycarbogermanes containing 1,4-bis(thiophenyl)buta-1,3-diyne is outlined in Scheme 2. The monomer **1** was treated with *n*-butyllithium at -78 °C to give the dilithiated intermediate, followed by co-polymerizations with R_2GeCl_2 ($R=Me, Ph$) in situ to yield the polycarbogermanes of poly[[1,4-bis(thiophenyl)buta-1,3-diyne]-*alt*-(dimethylgermane)] (**3**) and poly[[1,4-bis(thiophenyl)-



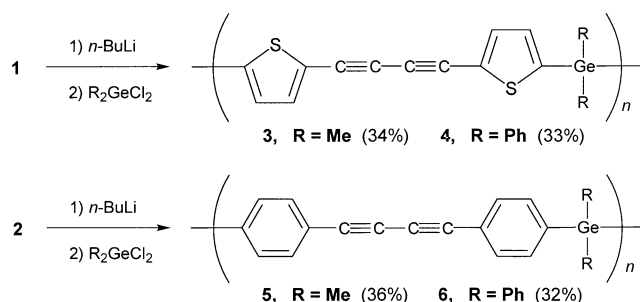
Scheme 1

buta-1,3-diyne]-*alt*-(diphenylgermane)] (**4**). The material **3** was obtained in reasonable yield as a dark brownish powder with a number-average molecular weight (M_n) of 5.40×10^3 and a polydispersity (M_w/M_n) of 3.67. **4** was also obtained as a brown powder with M_n of 3.06×10^3 and a polydispersity of 3.01.

The co-polymerizations of the lithiated **2** with R_2GeCl_2 ($R=Me, Ph$) were carried out in an identical way for the syntheses of **3** and **4** to yield the polycarbogermanes of poly[[1,4-bis(phenyl)buta-1,3-diyne]-*alt*-(dimethylgermane)] (**5**) and poly[[1,4-bis(phenyl)buta-1,3-diyne]-*alt*-(diphenylgermane)] (**6**), respectively (Scheme 2). **5** was obtained in reasonable yield as a brown powder with M_n of 6.48×10^3 and a polydispersity of 2.95. **6** was obtained as a dark yellowish powder with M_n of 8.50×10^2 and a polydispersity of 1.01.

All the materials have been also characterized by ¹H NMR and IR spectra. The selected spectral data of **3**, **4**, **5**, and **6** are summarized in Table 1. In particular, the characteristic C≡C stretching frequencies are observed at 2140–2180 cm^{-1} in the IR spectra of **3–6**, indicating that the diacetylene groups remain intact during polymerization reactions.

Properties of Polymers. The solubility of all the polymers **3**, **4**, **5**, and **6** in THF and chloroform allows us to perform studies on the properties in solution. The UV-visible absorption spectrum of **3** in THF is shown in Figure 1. The



Scheme 2

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Table 1. Some Properties of the Polymers **3**, **4**, **5**, and **6**

polymer	M_n^a	M_w/M_n^a	$^1\text{H NMR } \delta$ (ppm)	IR $\nu_{\text{C}=\text{C}}$ (cm^{-1})	UV-vis absorbance ^b λ_{max} (nm)	Fluorescence ^{b,c} λ_{max} (nm)	TGA ^d
3	5.40×10^5	3.67	0.8-1.0(br). 7.0-7.8(br)	2140	355	566	82
4	3.06×10^5	3.01	7.2-7.8(m)	2180	353	504	88
5	6.48×10^5	2.95	1.0-1.2(br). 7.2-7.8(br)	2175	318	457	90
6	8.50×10^5	1.01	7.0-7.6(m)	2150	314	406	55

^aDetermined by GPC in THF relative to polystyrene standards. ^bIn THF. ^cExcited at 298 nm. ^d% Weight remaining at 400 °C in nitrogen.

absorbance band centered at the λ_{max} of 355 nm appears with a molar absorptivity of $3.70 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$. The absorbance band centered at the λ_{max} of 353 nm in the UV-visible spectrum of **4** appears also with a molar absorptivity of $5.05 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ as shown in Figure 2. The strong absorbance bands with the high absorptivities of **3** and **4** might be attributed to the chromophores such as thiophene, diacetylene, and organogermane groups along the polymer backbone.

The fluorescence emission spectra of **3** and **4** at the excitation wavelength of 298 nm in THF are shown as the dotted lines in Figure 1 and 2, respectively. The fluorescence spectra of **3** and **4** show the strong emission peaks at the λ_{max} of 566 nm with the emission band of 391-785 nm and at the λ_{max} of 504 nm with the emission band of 365-756 nm, respectively. These strong emission peaks might be due to the chromophores of π -conjugated system in the polymers **3** and **4** along the polymer main chain.

Furthermore, the observed broadness of the absorption and emission spectra includes an important application respect in electro-optic field as white light continuum generation. Such phenomenon usually depends on the several factors that would be the inhomogenities in the number of repeating units of the prepared polymers, electronic energy dynamics of π -conjugation along the polymer backbone containing Ge atoms, and geometrical molecular structures in their electronic ground and/or excited states.

The UV-visible spectrum of **5** in THF shows that the strong absorbance band centered at the λ_{max} of 318 nm appears with a molar absorptivity of $5.00 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$. The fluorescence spectrum of **5** at the excitation wavelength of 298 nm

in THF shows a strong emission peak at the λ_{max} of 457 nm with the emission band of 361-687 nm. Both the strong absorption and emission peaks might be also attributed to the π -conjugated system in polymer **5** through the polymer main chain.

The thermal stabilities of polymers **3**, **4**, **5**, and **6** in nitrogen atmosphere were determined by thermogravimetric analysis (TGA). Typical TGA thermogram of **3** in nitrogen is shown in Figure 3. Polymer **3** is thermally stable up to 200 °C. Rapid weight loss of 35% occurs between 200 and 600 °C. When **3** is heated to 900 °C, a residue of 51% remains. Polymer **4** is thermally stable to 200 °C. Rapid weight loss of

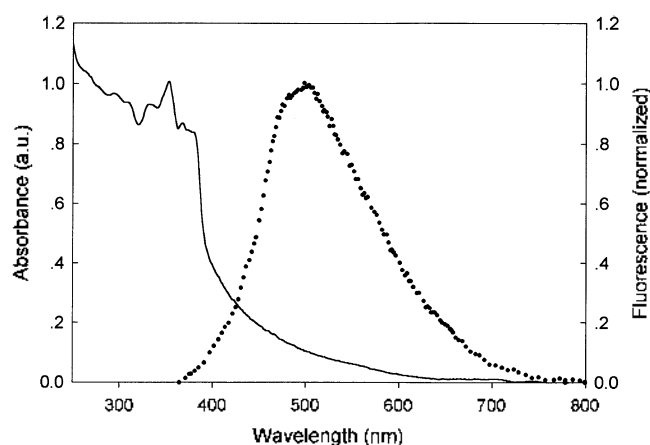


Figure 2. UV-vis absorption (—) and fluorescence emission (· · ·) spectra of **4** in THF.

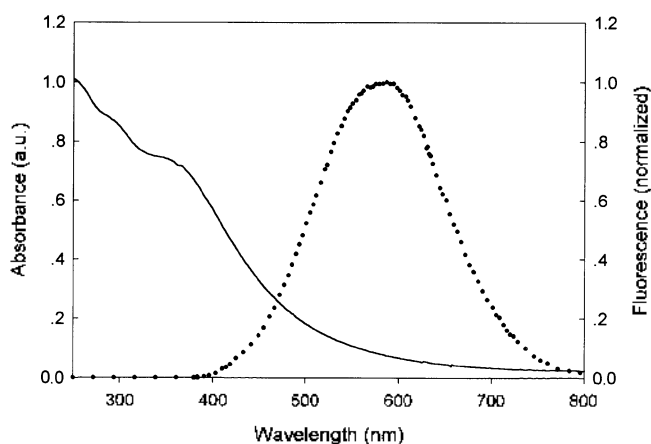


Figure 1. UV-vis absorption (—) and fluorescence emission (· · ·) spectra of **3** in THF.

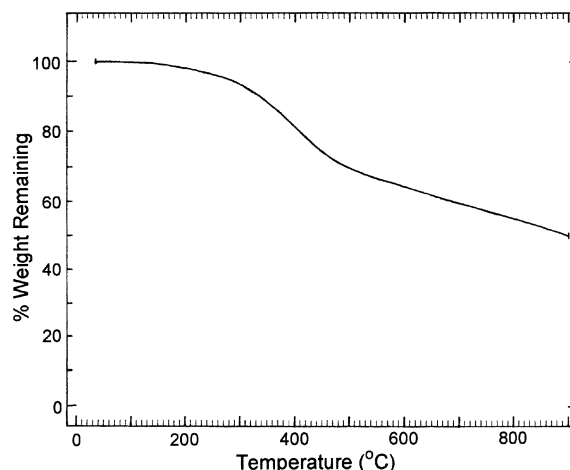


Figure 3. TGA thermogram of **3** in nitrogen.

33% occurs between 200 and 600 °C. At 900 °C, 52% of the initial sample weight of **4** remains. Polymer **5** was thermally stable to 200 °C. Rapid weight loss of 33% occurs between 200 and 600 °C. By 900 °C, 59% of the initial sample weight of **5** is still present. Oligomer **6** is thermally stable to 200 °C. Rapid weight loss of 45% occurs between 200 and 350 °C. At 900 °C, 65% of the initial sample weight of **6** is lost. All of the prepared materials **3-6** are thermally stable up to 200 °C under nitrogen atmosphere. The percent weight remaining at 400 °C in nitrogen for each polymer is also indicated in Table 1.

On the differential scanning calorimetry (DSC) curves of the obtained polymers, the anticipated exothermic peaks due to the cross-linking of diacetylene group were not observed, while the exothermic ones were reported in the diacetylene-containing organic polymers such as poly(2,5-diethynylthiophene)¹³ as well as the co-polymer of 1,4-bis(4-fluorophenyl)buta-1,3-diyne and hexafluorobisphenol-A.¹⁴ However, some glass-transition temperatures (T_g) were observed on the DSC curves of the polymers in nitrogen atmosphere. The polymers **3** and **6** demonstrate the T_g values at 314 and 309 °C, respectively.

In conclusion, polycarbogermans containing 1,4-bis(thiophene or phenylene)buta-1,3-diyne in the polymer backbone have been prepared. All of these materials are soluble in THF along with chloroform and are thermally stable up to 200 °C under nitrogen. UV-visible spectra exhibit the absorption λ_{max} values in the range of 314-355 nm. Fluorescence spectra show the emission λ_{max} values in the range of 406-566 nm. Both strong absorption and emission spectra indicate that the obtained polycarbogermans may be conjugated along the polymer main chain. By using an ultrafast fluorescence spectroscopy, the polymers are being investigated to understand the molecular energy dynamics.

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. ¹H and ¹³C NMR spectra were recorded on a JEOL JNM-EX90A. Chemical shifts were measured using tetramethylsilane or the solvent as internal standards. IR spectra were recorded a Bruker IFS-48 FT-IR spectrometer. UV-visible spectra were run on a Hewlett Packard 8452A spectrophotometer. Fluorescence emission spectra were obtained on a Hitachi F-2000 spectrofluorometer. 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 elutant 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 °C 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) and **1,4-bis(4-chlorophenyl)buta-1,3-diyne (2)** were prepared from 2-bromo-5-chlorothiophene and 4-bromochlorobenzene, respectively, according to the previously reported method.¹¹

Poly[[1,4-bis(thiophenyl)buta-1,3-diyne]-*alt*-(dimethylgermane)] (3). A flame dried 100 mL three-necked round bottom flask equipped with reflux condenser, pressure equalizing addition funnel, and a Teflon covered magnetic stirring bar was cooled to -78 °C using a dry-ice/acetone bath under argon atmosphere and then *n*-BuLi (2.5 M/hexane, 1.7 mL, 4.1 mmol) and THF (15 mL) were added. **1** (0.50 g, 1.8 mmol) and THF (15 mL) were placed in the addition funnel. This solution was slowly added to the flask with vigorous stirring. The reaction mixture was again cooled to -78 °C and Me₂GeCl₂ (0.31 g, 1.8 mmol) was added with well stirring at -78 °C for 2 h. The reaction mixture was allowed to warm to room temperature with stirring for 5 h. The crude product was precipitated by the addition of methanol and 10% aqueous HCl (20-30 mL) and isolated by decantation. The crude polymer was redissolved in THF (50-70 mL), washed with 10% aqueous HCl, deionized water, and concentrated at reduced pressure. The polymer was reprecipitated by addition of methanol (50-100 mL) and dried under reduced pressure. Polymer **3**, 0.19 g, 34% was obtained as a dark brownish powder with 19,800/5,400 (M_w/M_n). ¹H NMR (CDCl₃, 90 MHz): δ 0.8-1.0 (br, 6H), 7.0-7.8 (br, 4H); IR (KBr pallet): ν 3080, 2960, 2870, 2140 (C≡C), 1650, 1480, 1430, 1210, 1090, 995, 960, 800, 740, 690 cm⁻¹; UV-vis (THF) λ_{max} , nm (ϵ): 355 (3.70 × 10³). Anal. Calcd for (C₁₄H₁₀S₂Ge)_n: C, 53.39; H, 3.20; S, 20.36. Found: C, 55.59; H, 3.64; S, 21.83.

Poly[[1,4-bis(thiophenyl)buta-1,3-diyne]-*alt*-(diphenylgermane)] (4). **4** was prepared in an identical manner as **3**, using **1** (0.50 g, 1.8 mmol) and Ph₂GeCl₂ (0.54 g, 1.8 mmol). A brown powder, 0.25 g, 33% was obtained; $M_w/M_n=9.220/3.060$. ¹H NMR (THF-d₈, 90 MHz): δ 7.2-7.8 (m); IR (KBr pallet): ν 3100, 2960, 2870, 2180 (C≡C), 1645, 1425, 1260, 1210, 1065, 995, 800, 695 cm⁻¹; UV-vis (THF) λ_{max} , nm (ϵ): 353 (5.05 × 10³). Anal. Calcd for (C₂₄H₁₄S₂Ge)_n: C, 65.65; H, 3.21; S, 14.61. Found: C, 66.95; H, 3.82; S, 14.15.

Poly[[1,4-bis(phenyl)buta-1,3-diyne]-*alt*-(dimethylgermane)] (5). **5** was prepared in an identical manner as **3**, using **2** (0.51 g, 1.9 mmol) and Me₂GeCl₂ (0.34 g, 1.9 mmol). A brown powder, 0.20 g, 36% was obtained; $M_w/M_n=19.140/6.480$. ¹H NMR (THF-d₈, 90 MHz): δ 1.0-1.2 (br, 6H), 7.2-7.8 (br, 4H); IR (KBr pallet): ν 3080, 2960, 2870, 2175 (C≡C), 1660, 1585, 1475, 1385, 1260, 1090, 1010, 820, 690 cm⁻¹; UV-vis (THF) λ_{max} , nm (ϵ): 318 (5.00 × 10³). Anal. Calcd for (C₁₈H₁₄Ge)_n: C, 71.37; H, 4.66. Found: C, 71.88; H, 4.74.

Poly[[1,4-bis(phenyl)buta-1,3-diyne]-*alt*-(diphenylgermane)] (6). **6** was prepared in an identical manner as **3**, using **2** (0.50 g, 1.8 mmol) and Ph₂GeCl₂ (0.54 g, 1.8 mmol). A dark yellowish powder, 0.25 g, 32% was obtained; $M_w/M_n=880/850$. ¹H NMR (THF-d₈, 90 MHz): δ 7.0-7.6 (m); IR

(KBr pallet): ν 3090, 2150 (C \equiv C), 1640, 1585, 1480, 1460, 1385, 1090, 1010, 820, 785, 700 cm^{-1} ; UV-vis (THF) λ_{max} , nm (ϵ): 314 (5.00×10^3). Anal. Calcd for (C₂₈H₁₈Ge)_n: C, 78.75; H, 4.25. Found: C, 78.54; H, 4.11.

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