

Synthesis and Properties of Conjugated Polycarbosilanes with 1,4-Bis(thiophene or phenylene)-buta-1,3-diyne

Il Kwon Seo, Young Tae Park,* and Yong-Rok Kim†

Department of Chemistry, Keimyung University, Taegu 704-701, Korea

†Department of Chemistry, Yonsei University, Seoul 120-749, Korea

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Conjugated polycarbosilanes with diacetylene and aromatic groups of thiophene or phenylene simultaneously present in the polymer backbone such as poly[[1,4-bis(thiophenyl)buta-1,3-diyne]-*alt*-(dimethylsilane)], poly[[1,4-bis(thiophenyl)buta-1,3-diyne]-*alt*-(diphenylsilane)], poly[[1,4-bis(phenyl)buta-1,3-diyne]-*alt*-(dimethylsilane)], and poly[[1,4-bis(phenyl)buta-1,3-diyne]-*alt*-(diphenylsilane)] have been prepared. The characteristic C—C stretching frequencies appear at 2177–2179 cm^{-1} in the IR spectra of the polymers. The molecular weights of these polymers were determined by GPC. All of these materials are soluble in organic solvents such as THF and chloroform, and thermally stable up to 200 °C in general without any weight loss under nitrogen. The prepared materials in THF solvent show a maximum absorption peak in the range of 334–356 nm with a molar absorptivity of 10^3 – 10^5 L/(cm·mol) in the UV-visible absorption spectra. A maximum emission peak in the range of 403–550 nm is also observed in the fluorescence emission spectra. Both absorption and emission spectra strongly indicate that the obtained polycarbosilanes contain the new conjugated systems along the polymer main chain.

Introduction

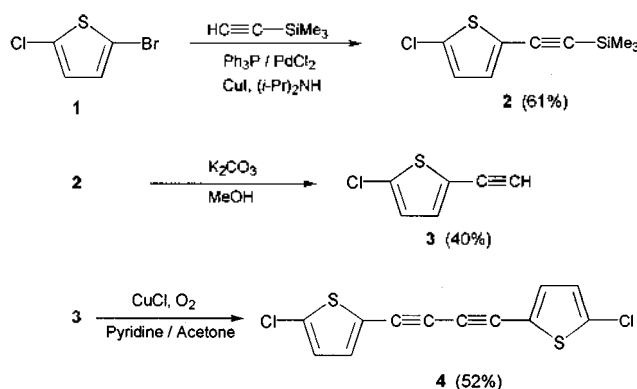
Conjugated polymers have received considerable attention for the potential applications of electrical and optical materials in recent years.¹ Conjugated organic polymers such as polyethynyl aromatics show electrical conductivity and high thermal stability upon heating, which indicates the possibility for electronic applications.^{2–4} It was found that conjugated polycarbosilanes of poly(silylenediacetylenes) have also shown conductivity as well as high thermal properties.^{5,6} Silicon-containing poly(*p*-phenylenevinylene) copolymers showed tunable electroluminescence for the possible application to blue light-emitting diodes.⁷ Synthesis and properties of polymers composed of regularly alternating organo-silicon and conjugated carbon groups have been reviewed in recent years.^{8,9} We have previously reported the synthesis and properties of low molecular weight of π -conjugated polythiophenes with diacetylene group as well as their molecular energy dynamics by using ultrafast fluorescence spectroscopy.^{10,11} To our knowledge, few polycarbosilanes conjugated with diacetylene and aromatic groups of thiophene or phenylene simultaneously present in the polymer backbone have been reported.

Herein we wish to represent the synthesis of new conjugated polycarbosilanes with 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

Synthesis of Monomers. The synthetic route for the monomer of 1,4-bis(5-chlorothiophene)-buta-1,3-diyne (**4**) is outlined in Scheme 1.

The synthesis of **4** involves three steps: (a) the displace-

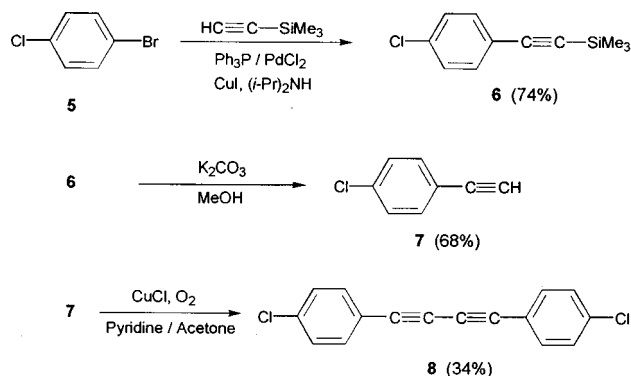


Scheme 1

ment of bromine of 2-bromo-5-chlorothiophene (**1**) with trimethylsilylacetylene. (b) the cleavage of the trimethylsilyl group, and (c) the oxidative coupling reaction. Trimethylsilylacetylene easily displaced only the bromine of **1** via a Heck-type reaction in the presence of palladium(II) chloride, triphenylphosphine, copper(I) iodide, and diisopropylamine to yield 2-(trimethylsilylethynyl)-5-chlorothiophene (**2**).^{12,13} The desilylation reaction of **2** was accomplished with potassium carbonate in methanol at room temperature to afford 2-ethynyl-5-chlorothiophene (**3**). The Glaser oxidative coupling reaction of **3** was carried out by using a co-solvent of acetone and pyridine (10 : 1 in v/v) in the presence of cuprous chloride with oxygen bubbling through the reaction mixture to yield the monomer **4**.¹³

The other monomer of 1,4-bis(4-chlorophenyl)-buta-1,3-diyne (**8**) was easily synthesized by the identical procedure to that for the monomer **4**, using 4-bromochlorobenzene (**5**) as starting material as shown in Scheme 2.

All of the prepared compounds were characterized by using several spectroscopic methods such as ¹H, ¹³C NMR,

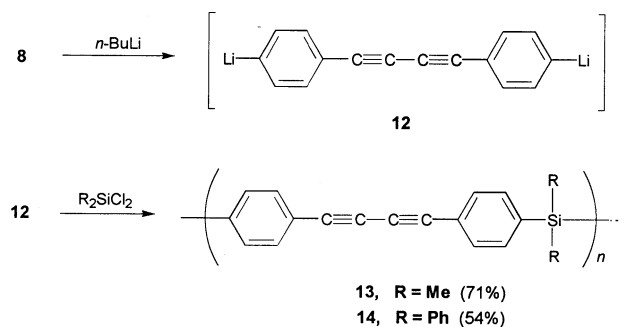
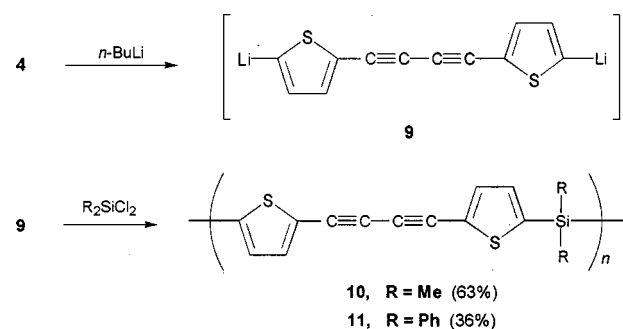


mass, and IR spectra as well as elemental analyses. Especially, the IR spectra show that the characteristic C=C stretching frequencies appear at 2108-2161 cm^{-1} .^{14,15}

Synthesis of Polymers. The synthetic route for the polycarbosilane containing 1,4-bis(thiophene)buta-1,3-diyne is outlined in Scheme 3.

The monomer **4** was treated with *n*-butyllithium at -78°C to give the dilithiated product of 1,4-bis(5-lithiothiophene)buta-1,3-diyne (**9**), followed by co-polymerizations with R_2SiCl_2 (R = Me, Ph) *in situ* to yield the polycarbosilanes such as poly[[1,4-bis(thiophenyl)buta-1,3-diyne]-*alt*-(dimethylsilane)] (**10**) and poly[[1,4-bis(thiophenyl)buta-1,3-diyne]-*alt*-(diphenylsilane)] (**11**), respectively. The oligomeric compound **10** was obtained in good yield as a dark yellowish powder with a molecular weight of 900/600-21,600/2,200 (M_w/M_n). The oligomer **11** was obtained as a brown powder with a molecular weight of 5,300/2,300-22,700/5,700 (M_w/M_n).

The co-polymerizations of the lithiated **8**, 1,4-bis(4-lithiophenyl)buta-1,3-diyne (**12**), with R_2SiCl_2 (R = Me, Ph) were carried out in an identical way for the oligomers **10**



and **11** to yield the polycarbosilanes such as poly[[1,4-bis(phenyl)buta-1,3-diyne]-*alt*-(dimethylsilane)] (**13**) and poly[[1,4-bis(phenyl)buta-1,3-diyne]-*alt*-(diphenylsilane)] (**14**), respectively, as shown in Scheme 4.

The oligomer **13** was obtained in high yield as a brown powder with a molecular weight of 25,000/4,300 (M_w/M_n). The oligomer **14** was obtained as a yellow powder with a molecular weight of 710/630-810/510 (M_w/M_n).

Each of the polymers has been also characterized by ^1H NMR and IR spectra as well as elemental analysis. The selected spectral data of the polymers **10**, **11**, **13**, and **14** are summarized in Table I.

In particular, the characteristic C=C stretching frequencies are observed at 2177-2179 cm^{-1} in the IR spectra of **10**, **11**, **13**, and **14**, indicating that the diacetylene groups are kept intact during polymerization reactions.

Properties of Polymers. The solubility of all the prepared polymers **10**, **11**, **13**, and **14** in THF and chloroform allows us to perform studies on the properties in solution phase. The UV-visible absorption spectrum of **10** in THF was shown in Figure 1.

The maximum absorption band at 348 nm appears with a molar absorptivity of $3.39 \times 10^5 \text{ L}/(\text{mol}\cdot\text{cm})$. The UV-visible spectrum of **11** in THF was also shown in Figure 2.

The maximum absorption band at 354 nm appears also with a molar absorptivity of $2.00 \times 10^5 \text{ L}/(\text{mol}\cdot\text{cm})$. The strong absorption bands with the high absorptivities of **10** and **11** might be attributed to the π -conjugation of thiophene, diacetylene, and organosilicon groups along the polymer backbone.

The fluorescence emission spectra of **10** and **11** at the excitation wavelength of 300 nm in THF solution were shown as the dotted lines in Figure 1 and 2, respectively. The fluorescence spectra of **10** and **11** show maximum emission peaks centered at 490 nm with the broad emission band of

Table I. Selected Spectral Data of the Polymers **10**, **11**, **13**, and **14**

polymer	^1H NMR δ (ppm)	IR $\nu(\text{C}=\text{C})$ (cm^{-1})	UV-vis absorption ^a λ_{max} (nm)	Fluorescence ^{a,b} λ_{max} (nm)	TGA ^c
10	0.10 (s), 7.42-7.52 (m)	2179	348	490	88
11	6.82 (m), 7.13 (m)	2177	354	550	80
13	0.10 (s), 6.70-7.90 (m)	2179	356	467	88
14	7.32 (m), 7.45 (m)	2179	334	403	44

^aIn THF. ^bExcited at 300 or 340 nm. ^c% Weight remaining at 400 $^\circ\text{C}$ in nitrogen.

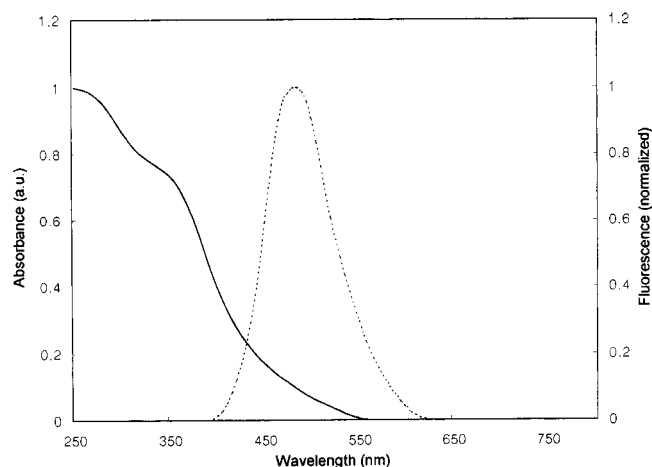


Figure 1. UV-visible absorption (—) and fluorescence emission (---) spectra of **10** in THF.

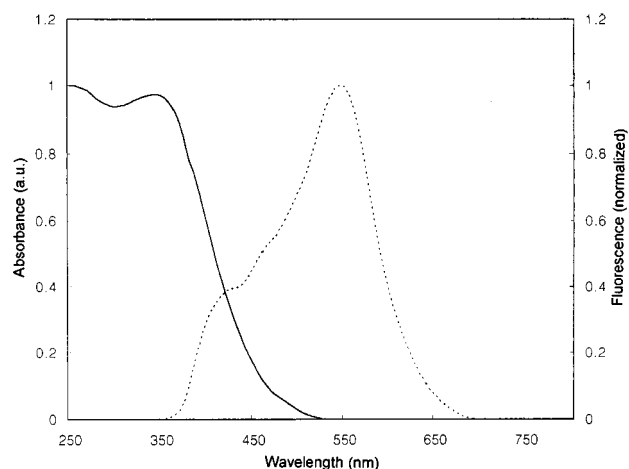


Figure 2. UV-visible absorption (—) and fluorescence emission (---) spectra of **11** in THF.

400–625 nm and at 550 nm with the broad emission band of 360–700 nm, respectively. These strong emission peaks might be due to the $\pi \rightarrow \pi^*$ transitions of π -conjugated system in the polymers **10** and **11** along the polymer main chain.

The UV-visible spectrum of **13** in THF shows that a maximum absorption band at 356 nm appears with a molar absorptivity of 5.18×10^5 L/(mol·cm). The fluorescence spectrum of **13** at the excitation wavelength of 340 nm in THF shows a maximum emission peak at 467 nm with the broad emission band of 350–630 nm. Both the strong absorption and emission peaks might be also attributed to the π -conjugated system in polymer **13** through the polymer main chain. The electronic spectral data of all the prepared polymers are summarized in Table I.

The thermal stabilities of polymers **10**, **11**, **13**, and **14** in nitrogen atmosphere were determined by thermogravimetric analysis (TGA). The typical TGA thermogram of **10** in nitrogen was shown in Figure 3.

10 is stable up to 245 °C without any weight loss. Rapid weight loss of 25% of the initial weight of **10** occurs between 300 and 580 °C. When the sample is heated to 900

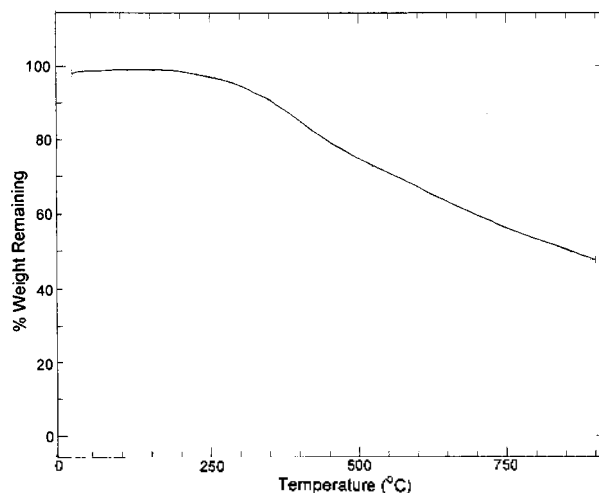


Figure 3. TGA thermogram of **10** in nitrogen.

°C, 51% of the initial weight of the sample is lost. Polymer **10** has glass-transition temperature (T_g) value in the range of 298–302 °C under nitrogen. **11** is stable up to 206 °C without any weight loss. Rapid weight loss of 43% of the initial weight of **11** occurs between 265 and 620 °C. When the sample is heated to 900 °C, 71% of the initial weight of the sample is lost. **13** is stable up to 215 °C without any weight loss. Rapid weight loss of 45% of the initial weight of **13** occurs between 315 and 695 °C. When the sample is heated to 900 °C, 60% of the initial weight of the sample is lost. **14** is stable up to 200 °C without any weight loss. Rapid weight loss of 53% of the initial weight of **14** occurs between 210 and 300 °C. When the sample is heated to 900 °C, 69% of the initial weight of the sample is lost. The prepared polymers **10–14** are usually stable up to 200 °C without any weight loss under nitrogen atmosphere.

Conclusion

Polycarbosilanes containing diacetylene as well as aromatic groups such as thiophene or phenylene in the polymer main chain have been prepared. The characteristic C—C stretching bands are found in all the IR spectra. All of these materials are soluble in THF and chloroform, and thermally stable up to 200 °C in general without any weight loss under nitrogen. The oligomeric materials in THF solvent show a maximum absorption peak in the range of 334–356 nm with a molar absorptivity of 10^3 – 10^5 L/(cm·mol) in UV-visible spectra. A maximum emission band in the range of 403–550 nm is also observed in the fluorescence spectra. Both absorption and emission spectra clearly indicate that the prepared polycarbosilanes contain the new conjugated systems along the polymer main chain. By using an ultrafast fluorescence spectroscopy, the molecular energy dynamics of the prepared polymers is under investigation.

Experimental Section

General Procedures. All chemicals were purchased

from Aldrich Chemicals Inc. Tetrahydrofuran (THF), *n*-hexane, *n*-pentane, and diethylether were distilled from sodium metal and benzophenone ketyl prior to use. Diisopropylamine was distilled from KOH before use. All glassware was dried over night in an oven at 120 °C. The apparatus was assembled and was then flame-dried while being swept with argon. All reactions were carried out under argon or nitrogen atmosphere. Reactions were monitored by analytical GLC of Hewlett Packard 5890 Series equipped with HP-1 capillary column (0.53 mm×30 m) coated with cross-linked methyl silicon gum and with flame ionization detector (FID). The column was deactivated immediately before use by injection of 50 μ L of hexamethyldisilazane. ¹H and ¹³C NMR spectra were recorded on a Bruker AM-300 spectrometer by using CDCl₃ as solvent. Chemical shifts were measured using tetramethylsilane or the solvent as internal standards. IR spectra were recorded on a Shimadzu IR 430 spectrometer or a Bruker IFS-48 FT-IR spectrometers. UV-visible spectra were measured with a Hewlett Packard 8452A or Shimadzu UV-106A spectrophotometer. Fluorescence emission spectra were obtained on a Hitachi F-2000 spectrofluorometer. Low resolution mass spectra were measured with a Hewlett Packard 5971A instrument by EI ionization at 70 eV. Gel permeation chromatography (GPC) analyses were performed on a Waters model 510 system with a Waters Styragel HR 3 column and refractive index detector. The eluting solvent was HPLC grade THF at a flow rate of 1.0 mL/min. The retention times were calibrated against known monodisperse polystyrene standard: *M_p* 580, 3250, 10100, and 28500 whose *M_w*/*M_n* are less than 1.2. Thermogravimetric analyses (TGA) of polymer samples were performed in nitrogen on a TGA-50 Shimadzu thermal analysis system. The temperature program for the analysis was from room temperature with a heating rate of 10 °C/min to 900 °C with nitrogen flow rate of 20 mL/min. Glass-transition temperatures were measured by differential scanning calorimetry in nitrogen on a Perkin-Elmer DSC-7. Elemental analyses were performed by a Fisons EA 1108 elemental analyzer at the Korea Basic Science Institute, Taegu, Korea.

5-Chloro-2-[(trimethylsilyl)-ethynyl]thiophene (2). In a flame dried 1L three-necked round bottom flask equipped with a mechanical stirrer and a reflux condenser were placed 2-bromo-5-chlorothiophene (**1**) (19.74 g, 0.10 mol), triphenylphosphine (1.75 g, 6.7 mmol), and diisopropylamine (200 mL) under argon atmosphere. Cuprous iodide (0.95 g, 5 mmol), trimethylsilylacetylene (11.79 g, 0.12 mol), palladium(II) chloride (0.15 g, 0.82 mmol), and diisopropylamine (200 mL) were added. The reaction mixture was warmed to 40 °C for 2 h and then heated to reflux for 12 h until GC analysis indicated that all starting material had disappeared. The solution was allowed to cool to room temperature and filtered to remove the precipitated diisopropylammonium bromide salt. The solvent was removed by evaporation under reduced pressure and the residue was taken up in methylenechloride. The organic layer was washed with 5% HCl solution, followed by water twice, dried over anhydrous MgSO₄, filtered, and concentrated at reduced pressure. The

crude product was dissolved in *n*-hexane and was purified by chromatography on a silica gel column. *n*-Hexane was used as the eluant. Compound **2**, 12.95 g, 61% was obtained. ¹H NMR (CDCl₃, 300 MHz) δ : 0.23 (s, 9H), 6.76 (d, 1H, *J* = 3.81 Hz), 6.99 (d, 1H, *J* = 3.81 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ : -0.26, 96.46, 99.41, 122.04, 126.10, 130.60, 132.07; IR (CCl₄ solution) ν : 2962.1, 2146.6 (C–C), 1538.2, 1428.7, 1251.3, 1161.6, 1065.7, 1005.2, 858.5, 833.1, 766.1 cm⁻¹; MS *m/z* (relative intensity) 216 (11.6), 215 (4.4), 214 (M⁺, 28.6), 201 (41.6), 200 (14.4), 199 (M⁺-Me, 100), 100 (4.8), 63 (6.9).

5-Chloro-2-ethynylthiophene (3). To a stirred solution of **2** (12.28 g, 59 mmol) and methanol (200 mL) in a flame dried 250 mL three-necked round bottom flask equipped with a reflux condenser, a gas inlet, and Teflon covered magnetic stirring bar was added K₂CO₃ (0.343 g, 2.4 mmol). The solution was stirred at room temperature for 3 h until GC analysis indicated that the reaction was complete. The reaction mixture was concentrated and *n*-pentane (40 mL) was added. The organic layer was washed with water (100 mL), dried over anhydrous MgSO₄, and filtered. The volatile solvent was removed by evaporation under reduced pressure. The residue was fractionally distilled. Compound **3**, 3.15 g, 40%, bp 30-32 °C/1.1 mmHg, was obtained. ¹H NMR (CDCl₃, 300 MHz) δ : 3.33 (s, 1H), 6.79 (d, 1H, *J* = 3.84 Hz), 7.05 (d, 1H, *J* = 4.07 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ : 76.0, 81.6, 120.7, 126.1, 131.0, 132.6; IR (CCl₄ solution) ν : 3311.5, 2959, 2928.2, 2872.8, 2107.5 (C–C), 1540.6, 1435.1, 1253, 1212, 1064, 995.5, 766.8 cm⁻¹; MS *m/z* (relative intensity) 114 (36), 142 (M⁺, 100), 107 (M⁺-Cl, 30), 82 (6), 69 (17), 63 (22).

1,4-Bis(5-chlorothiophenyl)-buta-1,3-diyne (4). In a flame dried 500 mL three-necked round bottom flask equipped with a reflux condenser, a addition funnel, a heating mantle, and Teflon covered magnetic stirring bar were placed CuCl (0.069 g, 0.70 mmol) and acetone 150-200 mL under argon atmosphere. The well stirred suspension was slowly warmed to 30 °C while the addition funnel was charged with a solution of acetone (20 mL) and pyridine (20 mL); 20 mL of this solution was added to the flask. The dark green mixture was stirred for 10 min before the compound **3** (1.0 g, 8.3 mmol) and 10 mL of the acetone/pyridine mixture were added. The mantle was removed when a small exotherm was observed. After a further stirring for 10 min, oxygen bubbling through the reaction mixture was begun. After the acetone/pyridine solution was added completely, a heating mantle was used to maintain the reaction temperature at 30-40 °C for an additional 6 h. The work-up was conducted under yellow light to prevent UV-induced cross-linking. The product was precipitated by the addition of methanol (20 mL) and 20% aqueous HCl (20 mL), and isolated by decantation. The crude product was redissolved in chloroform (100 mL), washed with 10% aqueous HCl and deionized water, dried over anhydrous MgSO₄, and filtered. The chloroform solution was concentrated, and the product was reprecipitated by addition of methanol (100 mL) and then dried under reduced pressure. Compound **4**, 0.59 g, 52%, mp

103–105 °C was obtained as a yellow powder. ^1H NMR (CDCl_3 , 300 MHz) δ : 6.82 (d, 2H, $J = 3.98$ Hz), 7.12 (d, 2H, $J = 3.96$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 76.1, 77.9, 120.5, 126.6, 132.5, 134.2; IR (KBr pallet) ν : 3097.3, 2141.8 (C–C), 1558.7, 1419.9, 1067.8, 997.8, 794 cm^{-1} ; MS m/z (relative intensity) 284 (80), 283 (19), 282 (M^+ , 100), 249 (8), 248 (3), 247 ($\text{M}^+ - \text{Cl}$, 19), 212 ($\text{M}^+ - \text{Cl}_2$, 11), 205 (18), 204 (8), 203 (44); Elemental Anal. Calcd for $\text{C}_{12}\text{H}_8\text{Cl}_2\text{S}_2$: C, 50.89; H, 1.42; S, 22.64. Found: C, 51.26; H, 1.34; S, 22.65.

1-Chloro-4-[(trimethylsilyl)ethynyl]benzene (6). In a flame dried 1L three-necked round bottom flask equipped with a mechanical stirrer and a reflux condenser were placed 4-bromochlorobenzene (**5**) (19.15 g, 0.10 mol), triphenylphosphine (1.75 g, 6.7 mmol), and diisopropylamine (150 mL) under argon atmosphere. Cuprous iodide (0.95 g, 5 mmol), trimethylsilylacetylene (11.79 g, 0.12 mol), palladium(II) chloride (0.15 g, 0.82 mmol), and diisopropylamine (150 mL) were added. The reaction mixture was warmed to 40 °C for 2 h and then heated to reflux for 12 h until GC analysis indicated that all starting material had disappeared. The solution was allowed to cool to room temperature and filtered to remove the precipitated diisopropylammonium bromide salt. The solvent was removed by evaporation under reduced pressure and the residue was taken up in methylenechloride. The organic layer was washed with 5% HCl solution, followed by water twice, dried over anhydrous MgSO_4 , filtered, and concentrated at reduced pressure. The crude product was dissolved in *n*-hexane and was purified by chromatography on a silica gel column. *n*-Hexane was used as the eluant. Compound **6**, 15.27 g, 74%, mp 48.1 °C was obtained. ^1H NMR (CDCl_3 , 300 MHz) δ : 0.24 (s, 9H), 7.27 (d, 2H, $J = 8.59$ Hz), 7.39 (d, 2H, $J = 8.62$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ : -0.12, 95.32, 103.79, 121.59, 128.52, 133.16, 134.47; IR (KBr pallet) ν : 2962.1, 2160.5 (C–C), 1558.2, 1488.5, 1251.2, 1161, 1092.5, 1015.7, 800.6, 630.6 cm^{-1} ; MS m/z (relative intensity) 210 (6.7), 209 (3.1), 208 (M^+ , 20.3), 195 (36.3), 194 (15.4), 193 ($\text{M}^+ - \text{Me}$, 100), 96 (3.8), 63 (7.5).

1-Chloro-4-ethynylbenzene (7). To a stirred solution of **6** (10 g, 48 mmol) in methanol (200 mL) in a flame dried 250 mL three-necked round bottom flask equipped with a reflux condenser, a gas inlet, and Teflon covered magnetic stirring bar was added K_2CO_3 (0.207 g, 1.5 mmol). The solution was stirred at room temperature for 3 h until GC analysis indicated that the reaction was complete. The reaction mixture was concentrated and *n*-pentane (40 mL) was added. The organic layer was washed with water (100 mL), dried over anhydrous MgSO_4 , and filtered. The volatile solvent was removed by evaporation under reduced pressure and the product was purified by recrystallization. Compound **7**, 6.18 g, 68%, mp 42.3 °C was obtained. ^1H NMR (CDCl_3 , 300 MHz) δ : 3.11 (s, 1H), 7.29 (d, 2H, $J = 8.81$ Hz), 7.42 (d, 2H, $J = 8.63$ Hz); ^{13}C -NMR (CDCl_3 , 75 MHz) δ : 78.15, 82.50, 120.57, 128.67, 133.3, 134.89; IR (KBr pallet) ν : 3312.7, 2958.1, 2927.3, 2871.9, 2107.5 (C–C), 1554.3, 1488.5, 1398.1, 1252.1, 1091.7, 1016.6, 766.6 cm^{-1} ; MS m/z (relative intensity) 138 (31.9), 137 (9.2), 136 (M^+ , 100), 102

(2.1), 101 ($\text{M}^+ - \text{Cl}$, 22.8), 100 (7.2), 75 (15.0), 74 (14.2).

1,4-Bis(4-chlorophenyl)-buta-1,3-diyne (8). In a flame dried 500 mL three-necked round bottom flask equipped with a reflux condenser, a addition funnel, a heating mantle, and Teflon covered magnetic stirring bar was placed CuCl (0.072 g, 0.7 mmol) and acetone 150–200 mL under argon atmosphere. The well stirred suspension was slowly heated to 30 °C while the addition funnel was charged with a solution of acetone (20 mL) and pyridine (20 mL); 20 mL of this solution was added to the flask. The dark green mixture was stirred for 10 min before the compound **7** (1.0 g, 8.3 mmol) and 10 mL of the acetone/pyridine mixture were added. The mantle was removed when a small exotherm was observed. After a further stirring for 10 min, oxygen bubbling through the reaction mixture was begun. After the acetone/pyridine solution was added completely, a heating mantle was used to maintain temperature at 30–40 °C for an additional 6 h. The work-up was conducted under yellow light to prevent UV-induced cross-linking. The product was precipitated by the addition of methanol (20 mL) and 20% aqueous HCl (20 mL), and isolated by decantation. The crude product was redissolved in chloroform (100 mL), washed with 10% aqueous HCl and deionized water, dried over anhydrous MgSO_4 , and filtered. The chloroform solution was concentrated, and the product was reprecipitated by addition of methanol (100 mL) and then dried under reduced pressure. Compound **8**, 3.28 g, 34%, mp 252–253 °C was obtained as a yellow powder. ^1H NMR (CDCl_3 , 300 MHz) δ : 7.31 (d, 2H, $J = 8.6$ Hz), 7.44 (d, 2H, $J = 8.6$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 74.83, 80.98, 120.39, 128.98, 133.76, 135.72; IR (KBr pallet) ν : 3083.6, 2150.2 (C–C), 1899.8, 1585.4, 1484.9, 1395.7, 1094.8, 1013.4, 821.0 cm^{-1} ; MS m/z (relative intensity) 274 (10.2), 273 (8.9), 272 (61.7), 271 (17.1), 270 (M^+ , 100), 200 ($\text{M}^+ - \text{Cl}_2$, 28), 199 (10.7); Elemental Anal. Calcd for $\text{C}_{16}\text{H}_8\text{Cl}_2$: C, 70.88; H, 2.97. Found: C, 70.49; H, 2.96.

Poly[[1,4-bis(thiophenyl)buta-1,3-diyne]-*alt*-(dimethylsilane)] (10). A flame dried 100 mL three-necked round bottom flask equipped with a reflux condenser, a pressure equalizing addition funnel, and Teflon covered magnetic stirring bar was cooled to -78 °C using a dry ice/acetone bath under argon atmosphere and then *n*-BuLi (1.6 M/hexane, 1.4 mL, 2.2 mmol) and THF (15 mL) were added. **4** (0.28 g, 1.0 mmol) and THF (15 mL) were placed in the addition funnel. This solution was slowly added to the flask with well stirring. The reaction mixture was allowed to stir at -78 °C for 2 h, and then warm to room temperature. The reaction mixture was again cooled to -78 °C and Me_2SiCl_2 (0.129 g, 1.0 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 **10**, 0.25 g,

63% was obtained as a dark yellowish powder. In this way, polymer **10** was obtained with a molecular weight of 900/600-21,600/2,200 (M_w/M_n). Thermal properties of **10** were described in the Results and Discussion. $^1\text{H NMR}$ (THF- d_6 , 300 MHz) δ : 0.10 (s, 6H), 7.42-7.52 (m, 4H); IR (KBr pallet) ν : 2960.5, 2179.2 (C=C), 1559, 1480, 1419.3, 1260, 995, 667.9 cm^{-1} ; Elemental Anal. Calcd for $(\text{C}_{14}\text{H}_{10}\text{S}_2\text{Si})_n$: C, 62.0; H, 3.7; S, 23.7. Found: C, 59.0; H, 3.8; S, 20.2; UV/Vis (THF) λ_{max} (nm) (ϵ in $\text{L}/(\text{cm}\cdot\text{mol})$): 290 (1.94×10^4), 348 (3.39×10^3).

Poly[[1,4-bis(thiophenyl)buta-1,3-diyne]-*alt*-(diphenylsilane)] (11). This compound was prepared by a procedure identical to that for polymer **10**, using **4** (0.5 g, 1.7 mmol) and Ph_2SiCl_2 (0.38 g, 1.7 mmol) instead of Me_2SiCl_2 . Polymer **11**, 0.25 g, 36% was obtained as a brown powder. In this way, polymer **11** was obtained with a molecular weight of 5,300/2,300-22,700/5,700 (M_w/M_n). TGA of **11** was described in the Results and Discussion. $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ : 6.82 (m), 7.13 (m); IR (KBr pallet) ν : 2956.9, 2176.7 (C=C), 1542, 1421.3, 1217.5, 1063.9, 997.1, 794.5, 668 cm^{-1} ; Elemental Anal. Calcd for $(\text{C}_{24}\text{H}_{14}\text{S}_2\text{Si})_n$: C, 73.0; H, 3.5; S, 16.2. Found: C, 74.3; H, 2.4; S, 18.2; UV/Vis (THF) λ_{max} (nm) (ϵ in $\text{L}/(\text{cm}\cdot\text{mol})$): 294 (2.96×10^5), 354 (2.00×10^5).

Poly[[1,4-bis(phenyl)buta-1,3-diyne]-*alt*-(dimethylsilane)] (13). A flame dried 100 mL three-necked round bottom flask equipped with a reflux condenser, a pressure equalizing addition funnel, and Teflon covered magnetic stirring bar was cooled to -78°C using a dry ice/acetone bath under argon atmosphere and then $n\text{-BuLi}$ (1.6 M/hexane, 2.8 mL, 4.4 mmol) and THF (15 mL) were added. **8** (0.54 g, 2.0 mmol) and THF (15 mL) were placed in the addition funnel. This solution was slowly added to the flask with well stirring. The reaction mixture was allowed to stir at -78°C for 2 h, and then warm to room temperature. The reaction mixture was again cooled to -78°C and Me_2SiCl_2 (0.25 g, 2.0 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 **13**, 0.37 g, 71% was obtained as a brown powder. In this way, polymer **13** was obtained with a molecular weight of 25,000/4,300 (M_w/M_n). TGA of **13** was described in the Results and Discussion. $^1\text{H NMR}$ (THF- d_6 , 300 MHz) δ : 0.10 (s, 6H), 6.70-7.90 (m, 8H); IR (KBr pallet) ν : 3080, 2956, 2929.8, 2970.8, 2179 (C=C), 1641.3, 1598.6, 1400.1, 1383.7, 1260.4, 1093.2, 1004.3, 827.7, 667.9 cm^{-1} ; Elemental Anal. Calcd for $(\text{C}_{18}\text{H}_{14}\text{Si})_n$: C, 83.6; H, 5.5. Found: C, 80.7; H, 5.8; UV/Vis (THF) λ_{max} (nm) (ϵ in $\text{L}/(\text{cm}\cdot\text{mol})$): 336 (5.18×10^5), 356

(5.18×10^5).

Poly[[1,4-bis(phenyl)buta-1,3-diyne]-*alt*-(diphenylsilane)] (14). This compound was prepared by a procedure identical to that for polymer **13**, using **8** (0.54 g, 2.0 mmol) and Ph_2SiCl_2 (0.43 g, 2.0 mmol) instead of Me_2SiCl_2 . Polymer **14**, 0.41 g, 54% was obtained as a yellow powder. In this way, polymer **14** was obtained with a molecular weight of 810/510-710/630 (M_w/M_n). TGA of **14** was described in the Results and Discussion. $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ : 7.32 (m), 7.45 (m); IR (KBr pallet) ν : 3084.5, 2179 (C=C), 1899.5, 1641.3, 1631.2, 1585.5, 1484.7, 1395.6, 1094.7, 1013.2, 821.9, 520.7 cm^{-1} ; Elemental Anal. Calcd for $(\text{C}_{28}\text{H}_{18}\text{Si})_n$: C, 87.9; H, 4.7. Found: C, 88.0; H, 5.4; UV/Vis (THF) λ_{max} (nm) (ϵ in $\text{L}/(\text{cm}\cdot\text{mol})$): 318 (2.68×10^4), 334 (2.90×10^4).

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