Hyperbranched Poly(2,5-silylthiophenes). The Possibility of σ−π Conjugation in Three Dimensions

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New hyperbranched organosilicon polymers have been prepared from 2-bromo-5-(trimethoxysilyl)thiophene. The intermediate alkoxy-substituted hyperbranched polymer is functionalized with Grignard reagents in situ, leading to the isolation of a series of air- and moisture-stable polymers. The polymers contain alternating silylene and thiophene groups along the branches and thus afford the possibility of σ−π conjugation in three dimensions. Investigations into the effects of this dimensionality utilize UV−visible spectroscopy.

Introduction

The synthesis of linear polymers containing alternating arrangements of silylene and π-electron moieties represents an area of current active interest. These polymers possess excellent potential as ceramic precursors,[1] heat-resistant materials,[2] semiconductors,[3] and photo- and electroluminescent materials.[4] The unusual electrical and optical properties associated with these materials are generally attributed to the delocalization of electrons through the silylene linkages. The specific nature of this delocalization is disputable, as evidenced by the various terms used to describe this phenomenon, including π−d_{Si} interactions,[5] π−$σ_{Si−Si}$ hyperconjugation,[6] and the more generally accepted σ−π conjugation. This delocalization is evidenced in these polymers by lower optical excitation energies compared to those found in analogous non-silicon-containing monomers and polymers.

Of particular interest are the poly(silylthiophenes),[7] polymers which consist of alternating silylene and thiophene groups along the backbone. These polymers generally exhibit enhanced electron delocalization along the polymer backbone and improved solubilities. The general electrical and optical properties of these polymers are well-known and demonstrate their potential use in many optoelectronic applications, including nonlinear optics.[8] *Hyperbranched* poly(silylthiophenes) are unknown[9] and would merit examination for a number of reasons.[10] These hyperbranched polymers could possess unique optoelectronic properties due to electron conjugation in *three dimensions,* as opposed to the one-dimensional conjugation in conventional linear poly(silylthiophenes). Furthermore, hyperbranched polymers are more soluble and processable than analogous linear polymers and are prepared in a one-step process from the monomer. In addition, hyperbranched poly-

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(1) For representative examples, see: (a) Ijadi-Maghsoodi, S.; Barton, T. J. *Macromolecules* **1990**, *23*, 4485. (b) Corriu, R. J. P.; Gerbier, P.; Guerin, C.; Henner, B. J. L.; Jean, A.; Mutin, P. H. *Organometallics* **1992**, *11*, 2507. (c) Pang, Y.; Ijadi-Maghsoodi, S.; Barton, T. J. *Macromolecules* **1993**, *26*, 5671. (d) Corriu, R. J. P.; Gerbier, P.; Guerin, C.; Henner, B. *J. Organomet. Chem.* **1993**, *449*, 111. (e) Ohshita, J.; Kanaya, D.; Watanabe, T.; Ishikawa, M. *J. Organomet. Chem.* **1995**, *489*, 165. (f) Pudelski, J. K.; Rulkens, R.; Foucher, D. A.; Lough, A. J.; MacDonald, P. M.; Manners, I. *Macromolecules* **1995**, *28*, 7301. (g) Corriu, R. J. P.; Devylder, N.; Guerin, C.; Henner, B.; Jean, A. *J. Organomet. Chem.* **1996**, *509*, 249.

(2) Itoh, M.; Inoue, K.; Iwata, K.; Mitsuzuka, M.; Kakigano, T. *Macromolecules* **1997**, *30*, 694.

(3) For representative examples, see: (a) Ishikawa, M.; Hasegawa, Y.; Kunai, A.; Yamanaka, T. *J. Organomet. Chem.* **1990**, *381*, C57. (b) Brefort, J. L.; Corriu, R. J. P.; Gerbier, P.; Guerin, C.; Henner, B. J. L.; Jean, A.; Kuhlmann, T. *Organometallics* **1992**, *11*, 2500. (c) Ishikawa, M.; Sakamoto, H.; Ishii, M.; Ohshita, J. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 3281. (d) Fang, M.-C.; Watanabe, A.; Matsuda, M. *Chem. Lett.* **1994**, 13. (e) Kunai, A.; Toyoda, E.; Horata, K.; Ishikawa, M. *Organometallics* **1995**, *14*, 714.

(4) (a) Fang, M.-C.; Watanabe, A.; Matsuda, M. *Macromolecules* **1996**, *29*, 6807. (b) Kim, H. K.; Ryu, M.-K.; Lee, S.-M. *Macromolecules* **1997**, *30*, 1236. (c) Li, H.; Powell, D. R.; Firman, T. K.; West, R. *Macromolecules* **1998**, *31*, 1093. (d) Kim, H. K.; Ryu, M.-K.; Kim, K.-D.; Lee, S.-M.; Cho, S.-W.; Park, J.-W. *Macromolecules* **1998**, *31*, 1114.

(5) (a) Shizuka, H.; Sato, Y.; Ueki, Y.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 341. (b) Sakurai, H.; Sugiyama, H.; Kira, M. *J. Phys. Chem.* **1990**, *94*, 1837. (c) Sakurai, H. *J. Organomet. Chem.* **1980**, *200*, 261.

(6) Egorochkin, A. N. *Russ. Chem. Rev. (Engl. Transl.)* **1984**, *53*, 445.

(7) For representative examples, see: (a) Hu, S.-S.; Weber, W. P. *Polym. Bull.* **1989**, *21*, 133. (b) Chicart, P.; Corriu, R. J. P.; Moreau, J. J. E.; Garnier, F.; Yassar, A. *Chem. Mater.* **1991**, *3*, 8. (c) Ohshita, J.; Kanaya, D.; Ishikawa, M.; Koike, T.; Yamanaka, T. *Macromolecules* **1991**, *24*, 2106. (d) Ritter, S. K.; Noftle, R. E. *Chem. Mater.* **1992**, *4*, 872. (e) Yi, S. H.; Nagase, J.; Sato, H. *Synth. Met.* **1993**, *58*, 353. (f) Yi, S.-H.; Ohashi, S.; Ogino, K.; Sato, H.; Nomori, H. *Synth. Met.* **1993**, *61*, 247. (g) Yuan, C.-H.; West, R. *Appl. Organomet. Chem.* **1994**, *8*, 423. (h) Tanaka, K.; Ago, H.; Yamabe, T.; Ishikawa, M.; Ueda, T. *Organometallics* **1994**, *13*, 3496. (i) Fang, M.-C.; Watanabe, A.; Matsuda, M. *J. Organomet. Chem.* **1995**, *489*, 15. (j) Herrema, J. K.; van Hutten, P. F.; Gill, R. E.; Wildeman, J.; Wieringa, R. H.; Hadziioannou, G. *Macromolecules* **1995**, *28*, 8102. (k) Kunai, A.; Ueda, T.; Horata, K.; Toyoda, E.; Nagamoto, I.; Ohshita, J.; Ishikawa, M. *Organometallics* **1996**, *15*, 2000. (l) Ago, H.; Kuga, T.; Yamabe, T.; Tanaka, K. *Chem. Mater.* **1997**, *9*, 1159. (m) Chen, R.-M.; Chien, K.-M.; Wong, K.-T.; Jin, B.-Y.; Luh, T.-Y. *J. Am. Chem. Soc.* **1997**, *119*, 11321. (n) Moreau, C.; Serien-Spirau, F.; Biran, C.; Bordeau, M.; Gerval, P. *Organometallics* **1998**, *17*, 2797.

(8) Moreau, C.; Serein-Spirau, F.; Letard, J.-F.; Lapouyade, R.; Jonusauskas, G.; Rulliere, C. *J. Phys. Chem. B* **1998**, *102*, 1487.

(9) While our work was in progress, the synthesis of small silylthiophene *dendrimers* was reported: Nakayama, J.; Lin, J.-S. *Tetrahedron Lett.* **1997**, *38*, 6043.

(10) For reviews and general aspects of hyperbranched polymers, see: (a) Bochkarev, M. N.; Katkova, M. A. *Russ. Chem. Rev. (Engl. Transl.)* **1995**, *64*, 1035. (b) Frechet, J. M. J.; Hawker, C. J. *Compr. Polym. Sci.* **1996**, 71 (2nd Suppl.). (c) Malmstrom, E.; Hult, A. *J. Mater. Sci.-Rev. Macromol. Chem. Phys.* **1997**, *C37*, 555. (d) Kim, Y. H. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1685.

Scheme 1
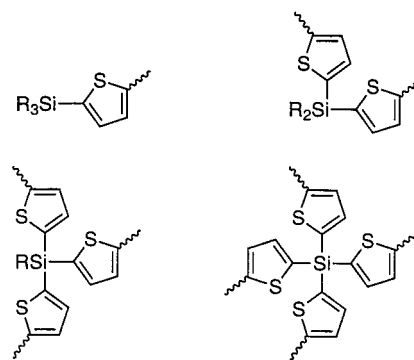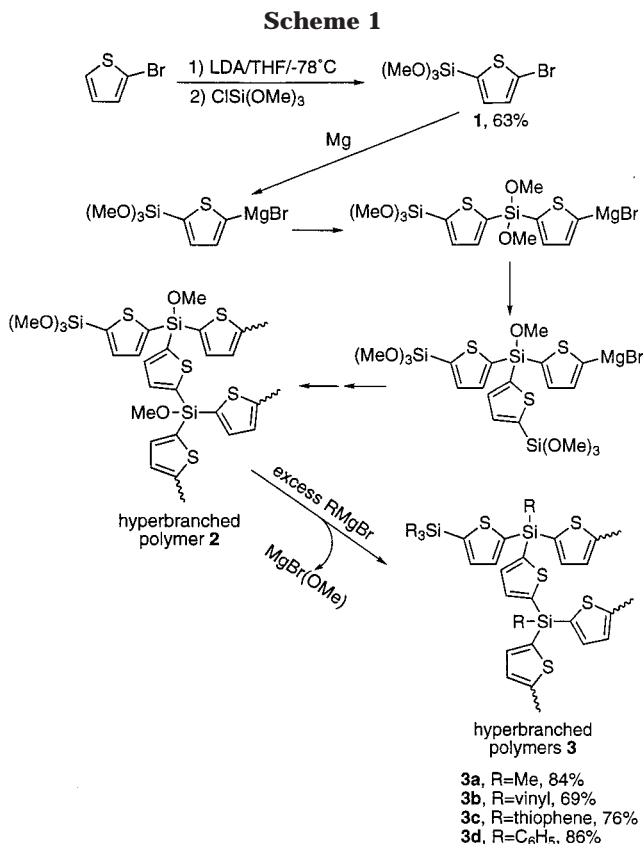
Figure 1. The four possible local environments of the silicon atoms in **2**. R = OMe (**2**), Me (**3a**), vinyl (**3b**), thiophene (**3c**), C_6H_5 (**3d**).

merization leaves many functional sites along the branches unreacted in the final polymer. The advantages of hyperbranched poly(silylthiophenes) would thus be ease of synthesis, improved processability, and more importantly, the possibility of *tuning* certain properties such as optical absorbances and solubility by simple manipulation of the unreacted functional sites. Tunable polymers are desirable from an applications point of view, since properties can often be adjusted by simple modifications of polymer substituents or backbone composition.[11]

Numerous structural types of hyperbranched organosilicon polymers have been successfully prepared in recent years.[12] In this report we describe the synthesis and characterization of hyperbranched poly(2,5-silylthiophenes), representing a new structural class of $\sigma-\pi$ conjugated polymers.

Results and Discussion

Polymer Synthesis. The synthesis of hyperbranched poly(2,5-silylthiophenes) is outlined in Scheme 1. Selec-

tive deprotonation of 2-bromothiophene with LDA followed by reaction with chlorotrimethoxysilane yielded the AB_3 monomer **1** as a clear, colorless, moisture-sensitive liquid in 63% yield after distillation. Addition of **1** to magnesium turnings in THF resulted in rapid formation of the Grignard reagent, indicated by consumption of magnesium and a color change to dark brown. Polymerization then proceeds by random reactions of the carbanions with Si−OMe bonds in the reaction system to form new C−Si bonds (Scheme 1). After overnight refluxing, large amounts of the magnesium salt byproducts were present in the reaction mixture. Filtering off these solids along with excess magnesium turnings gave a solution of hyperbranched polymer **2** in THF.

Polymer **2** serves as the potential starting point for a wide range of substituted hyperbranched poly(2,5-silylthiophenes). By virtue of the reactive methoxy groups present in the polymer, various substituents can be attached to the branches by simply treating **2** with the appropriate nucleophilic reagent. To illustrate this concept, we treated separate solutions of **2**[13] with methyl, vinyl, thiophene, and phenyl Grignard reagents (Scheme 1). The resulting fully substituted polymers **3a**−**d** were obtained in good to excellent yields after precipitation from methanol.

Due to the nature of polymerization, the resulting polymers possess random, highly branched structures. The structures shown in Scheme 1 are purely hypothetical and do not necessarily reflect an actual polymer structure. In reality the Si atoms in the polymer serve as branch points and exist in any of four possible local environments, as shown in Figure 1. The branched nature of these polymers can be confirmed by NMR spectroscopy. The ^1H NMR spectrum of **3a** (Figure 2) shows that, in addition to the set of peaks corresponding to the thiophene protons (δ 7.3−7.5), three large separate peaks are apparent at δ 0.33, 0.64, and 0.95. These peaks correspond quite well to the methyl proton chemical shifts in small-molecule model compounds[14−16] (Figure 3), which in turn correspond to the different

(11) (a) Berggren, M.; Inganas, O.; Gustafsson, G.; Rasmusson, J.; Anderson, M. R.; Hjertberg, T.; Wennerstrom, O. *Nature* **1991**, *372*, 444. (b) Banovetz, J. P.; Hsiao, Y.-L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 2540. (c) Hsiao, Y.-L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1994**, *116*, 9779. (d) Allcock, H. R. *Adv. Mater.* **1994**, *2*, 106. (e) Zechel, D. L.; Hultzsch, K. C.; Rulkens, R.; Balaishis, D.; Ni, Y.; Pudelski, J. K.; Lough, A. J.; Manners, I.; Foucher, D. A. *Organometallics* **1996**, *15*, 1972. (f) Nguyen, P.; Lough, A. J.; Manners, I. *Macromol. Rapid Commun.* **1997**, *18*, 953. (g) Rushkin, I. L.; Shen, Q.; Lehman, S. E.; Interrante, L. V. *Macromolecules* **1997**, *30*, 3141. (h) Kobayashi, T.; Hatayama, K.; Suzuki, S.; Abe, M.; Watanabe, H.; Kijima, M.; Shirakawa, H. *Organometallics* **1998**, *17*, 1646. (i) Lucht, B. L.; Mao, S. S. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 4354.

(12) For early examples of hyperbranched poly(carbosilanes), see: (a) Whitmarsh, C. K.; Interrante, L. V. *Organometallics* **1991**, *10*, 1336. (b) Muzafarov, A. M.; Gorbatsevich, O. B.; Rebrov, E. A.; Ignat'eva, G. M.; Chenskaya, T. B.; Myakushev, V. D.; Bulkin, A. F.; Papkov, V. S. *Polym. Sci.* **1993**, *35*, 1575; *Vysokomol. Soedin.* **1993**, *35*, 1867.

(13) Although polymer **2** can be isolated, this procedure is rather tedious due to the moisture sensitivity of the Si−O bonds and the presence of magnesium salts still present in solution.
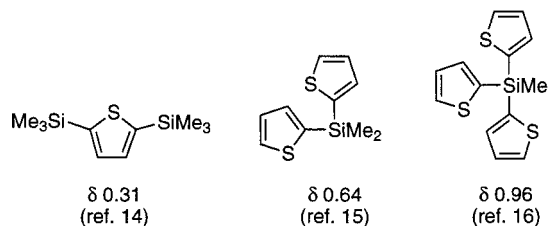
(14) Tour, J. M.; Wu, R. *Macromolecules* **1992**, *25*, 1901.

(15) Moreau, C.; Serein-Spirau, F.; Bordeau, M.; Biran, C.; Dunogues, J. *J. Organomet. Chem.* **1996**, *522*, 213.

(16) Lukevics, E.; Pudova, O. A.; Popelis, Y.; Erchak, N. P. *Zh. Obshch. Khim.* **1981**, *51*, 115.
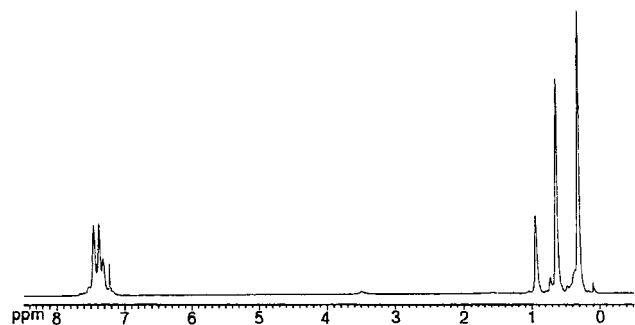
Figure 2. 400 MHz ^{1}H NMR spectrum of polymer **3a** (in CDCl$_3$).

δ 0.31
(ref. 14)

δ 0.64
(ref. 15)

δ 0.96
(ref. 16)

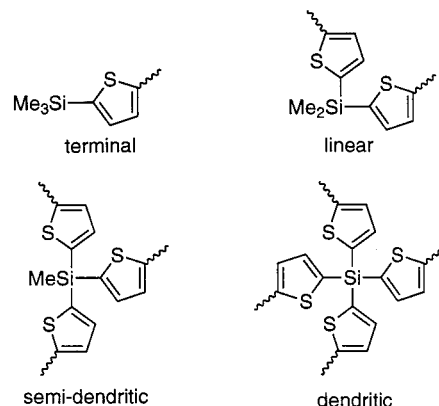**Figure 3.** Methyl proton ^{1}H NMR chemical shifts of known small compounds.

Table 1. Molecular Weight and Thermal Data for Polymers 3a−d

polymer	M_n (GPC)	M_w (GPC)	M_n (VPO)	thermal data (°C)
3a	4 458	10 552	4 190	43 (mp)
3b	6 587	67 535	10 480	14 (T_g)
3c	5 481	14 900	10 125	120 (T_g)
3d	5 425	16 166	9 216	135 (T_g)

types of branch points in the hyperbranched polymer. The branched nature of these polymers was also confirmed by ^{29}Si NMR spectroscopy, which indicated the presence of the four different types of silicon atoms.

Polymers **3a−d** were obtained as lightly colored solids after precipitation. Polymers **3a,c,d** were powdery in nature, while **3b** was slightly sticky at room temperature. These polymers are stable to air and moisture and can be stored without any special precautions. Polymers **3a,b** are very soluble in common organic solvents, including ethyl ether, THF, chloroform, and even hexane. Slightly different solubilities were observed for polymers **3c,d**, which are soluble in THF and CHCl$_3$, partially soluble in ethyl ether, and insoluble in hexane. Molecular weight data are detailed in Table 1 and indicate broad weight distributions, a common characteristic of hyperbranched polymers. We attribute the slightly high molecular weight observed for **3b** to partial cross-linking of the polymer. The GPC chromatogram for **3b** indicated a bimodal distribution, all of which was included in the overall MW calculation. The inclination for **3b** to undergo cross-linking was also evidenced by the eventual insolubility of **3b** on mild heating.

Determination of Degree of Branching (DB). The integration of the peaks in the **3a** ^{1}H NMR spectrum also allows the calculation of degree of branching[17] (DB) in these polymers by providing data on the relative amounts of each type of Si branch point. By definition, we can label the various types of silicon atoms in **3a** as shown in Figure 4.

(17) (a) Hawker, C. J.; Lee, R.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583. (b) Kim, Y. H. *Macromol. Symp.* **1994**, *77*, 21. (c) Holter, D.; Burgath, A.; Frey, H. *Acta Polym.* **1997**, *48*, 30.

Figure 4. Various silicon atom environments in **3a**.

A number of methods can be used to perform the DB calculation, but only one method will be presented here. Variables can be assigned as follows:

a = number of terminal silicon atoms

b = number of linear silicon atoms

c = number of semidendritic silicon atoms

d = number of dendritic silicon atoms

If we assume that we are examining 100 Si atoms of this polymer, we can write the four equations

$$(1) \quad a + b + c + d = 100$$

(2) $9a + 6b + 3c = 600$ (this counts the number of hydrogen atoms)

(3) $a/b = 0.7526$ (from the ^{1}H NMR integration)

(4) $b/c = 1.4388$ (from the ^{1}H NMR integration)

From these four equations this system can be solved. The results are

$$a = 30.4$$
$$b = 40.4$$
$$c = 28.1$$
$$d = 1.11$$

By definition,[17c] the DB in hyperbranched polymers obtained from AB$_3$ monomers is given by

$$DB = (2d + c)/[(2/3)(3d + 2c + b)]$$

Substituting the appropriate values gives DB = 0.46 for this hyperbranched polymer system. Theoretically, in a perfectly random hyperbranched polymer of this type, DB = 0.44.[17c] Thus, our obtained value is within reasonable limits. However, there is somewhat of a discrepancy in the ratios of each type of silicon atom. The theoretical ratios are a:b:c:d = 8:12:6:1. In our system, a:b:c:d = 27:36:25:1. Obviously, there is a decided lack of dendritic silicon atoms in our system. This also explains why the dendritic silicon atoms were often difficult to identify in the ^{29}Si NMR spectra of the polymers. This ratio difference may be explained from a sterics factor standpoint. The theoretical calculations assume that reactivity at the branch points is always constant, regardless of the degree of substitution on the
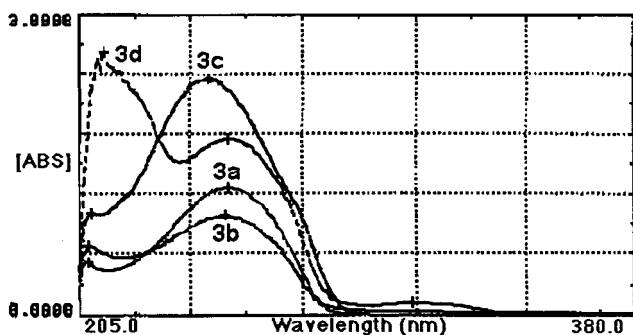
Figure 5. UV−visible spectra of **3a−d**.

Table 2. UV−Visible Data for Polymers 3a−d (in THF)

polymer	λ_{max} (nm)	ϵ (per average repeat unit)
3a	252	12 000
3b	251	13 900
3c	246	26 200
3d	213	19 100
	252	12 800

branch atom. In reality, steric factors play an important role in relative reactivity. Silicon atoms bonded to three thiophene groups are relatively hindered. Therefore, attack at those atoms by another thiophene nucleophile would not be as likely as it would be for silicon atoms bonded to one or two thiophene groups. Despite this lack of dendritic silicon atoms, the DB is still high due to the increased amount of semidendritic silicon atoms compared to theoretical amounts.

UV−Vis Spectroscopy. The extent of $\sigma-\pi$ conjugation in these polymers was examined using UV−visible spectroscopy. The spectra are shown in Figure 5, and the data are summarized in Table 2. The $\pi-\pi^*$ transitions in **3a−d** are significantly red-shifted compared to thiophene itself (230 nm), indicating a significant degree of conjugation through the silicon atoms. These absorptions appear to be relatively independent of the polymer substituents, save for thiophene, which resulted in a blue shift of approximately 6 nm in **3c**. The UV−visible spectra also indicated broad weak absorptions in the 300−320 nm region which are suggestive of charge transfer from thiophene to silicon.[8] The effects of the three-dimensional polymer structure versus a one-dimensional one are not yet entirely clear, but at least for the $\pi-\pi^*$ absorptions they appear to be relatively minor. The λ_{max} and extinction coefficient values for **3a−d** are similar to those obtained for linear polymers.[7d,e,i]

Conclusion. In conclusion, we have outlined the synthesis and characterization of new hyperbranched poly(2,5-silylthiophenes). These polymers represent a new structural class of $\sigma-\pi$ conjugated polymers and may possess unique and novel properties beyond those described above. Further investigations will elucidate these properties.

Experimental Section

Materials and General Comments. All reactions were performed under an atmosphere of dry N_2. The following reagents were obtained from commercial sources and used without further purification: 2-bromothiophene, magnesium turnings, vinyl bromide, bromobenzene, methylmagnesium bromide (3.0 M solution in ether), *n*-BuLi (hexane solution,

2.5 M), and diisopropylamine. Chlorotrimethoxysilane was prepared using a literature procedure.[18] Tetrahydrofuran (THF) was distilled from Na/benzophenone under a N_2 atmosphere prior to use.

The ${}^1H$, ${}^{13}C$, and ${}^{29}Si$ (INEPT) NMR spectra were performed on a 400 MHz Bruker ADVANCE DRX multinuclear NMR spectrometer using $CDCl_3$ as reference. Elemental analyses were obtained from E+R Microanalytical Laboratory, Corona, NY. Glass transition temperatures (T_g) and melting points were measured using a Dupont DSC Model 910 instrument equipped with a TA Operating Software Module and Data Analysis data station. Temperature was increased at a heating rate of 10 °C/min. Gel permeation chromatography measurements were performed on a Waters Associates GPC II instrument using 500, 10^4, 10^5, and 10^6 Å μ-Styragel columns and UV or refractive index detectors. The operating conditions consisted of a flow rate of 1.5 mL/min of unstabilized HPLC-grade THF containing 0.1% tetra-*n*-butylammonium bromide ((n-Bu)$_4$NBr), a column temperature of 30 °C, and a sample injection volume of 0.05−0.1 mL of a 0.1% solution. The system was calibrated with a series of narrow-molecular-weight polystyrene standards in the molecular weight range of ca. 10^3−10^6. Molecular weights were also obtained on a Wescan Instruments, Inc. Model 233 vapor pressure osmometer (VPO) instrument. UV−visible spectroscopy was performed on a Beckman DU 640 spectrophotometer. Samples were prepared in concentrations ranging from 0.0001 to 0.000 01 M in chloroform. Samples were scanned from 288 to 800 nm at a rate of 1200 nm/min. Data from these spectra are presented in the body of the paper.

Synthesis of 2-Bromo-5-trimethoxysilylthiophene (1). *n*-BuLi (58.0 mL, 145 mmol) was added to a round-bottomed flask containing diisopropylamine (17.6 g, 174 mmol) dissolved in THF (100 mL) chilled in a water/ice bath. The mixture was stirred for 30 min and then cooled in a dry ice/acetone bath. 2-Bromothiophene (28.4 g, 174 mmol) was then added dropwise. After the addition, the flask was placed in a salt/ice bath and stirred for 45 min. This solution was then transferred via cannula to another round-bottomed flask containing chlorotrimethoxysilane (29.4 g, 188 mmol) and THF (100 mL) chilled in a dry ice/acetone bath. The mixture was stirred in the dry ice/acetone bath and warmed to room temperature, at which point it was stirred overnight. Most of the solvents were removed under reduced pressure, and then pentane was added to the remainder, resulting in the formation of copious amounts of white precipitate. The suspension was filtered, and the filtrate was distilled to afford 25.7 g (63%) of **1** as a colorless liquid (65−66 °C/0.10 mmHg). ${}^1H$ NMR ($CDCl_3$): δ 7.11 (d, $J = 3.58$ Hz, 1H), 7.04 (d, $J = 3.52$ Hz, 1H), 3.52 (s, 9H). ${}^{13}C$ NMR ($CDCl_3$): δ 137.58, 131.40, 130.82, 119.07, 50.97. ${}^{29}Si\{{}^1H\}$: δ −60.1 ($J = 3.6$ Hz). Anal. Calcd for $C_7H_{11}O_3$-BrSiS: C, 29.69; H, 3.92. Found: C, 29.71; H, 3.89.

Synthesis of Hyperbranched Polymer 2. A 100-mL, three-necked round-bottomed flask was equipped with a reflux condenser, addition funnel, septum, and stir bar. Magnesium turnings (1.60 g, 65.8 mmol) were added and dry-stirred for 1 h. THF (5 mL) was then added. Compound **1** (6.66 g, 23.5 mmol) was then added dropwise from the addition funnel. During the addition, the reaction mixture turned brown and a precipitate formed. After completion of addition, additional THF (50 mL) was added. The mixture was then stirred for 2 h at room temperature and refluxed overnight. The suspension was filtered to give a solution of **2**, which was then used as is in further functionalization reactions.

Synthesis of Hyperbranched Polymer 3a. A solution of methylmagnesium bromide (30 mL, 90 mmol) was added dropwise to an ice-cold solution of **2** prepared from 6.66 g (23.5 mmol) of **1**. The mixture was stirred at room temperature

(18) Corriu, R. J. P.; Moreau, J. J. E.; Thepot, P.; Wong Chi Man, M. *Chem. Mater.* **1992**, *4*, 1217.

overnight. Methanol (20 mL) was then added to react with excess Grignard reagent. Most of the volatiles were removed under reduced pressure, and hexane (500 mL) was added to the filtrate. The suspension was filtered, and volatiles were removed from the filtrate under reduced pressure to give the crude product as a yellow sticky solid. The crude product was purified by dissolving in chloroform and precipitating into a large excess of methanol. Polymer **3a** was obtained as a white powder in 84% yield (2.76 g). Mp: 43 °C. Molecular weight: M_n 4458, M_w 10 552 (GPC, polydispersity 2.4); M_n 4190 (VPO). All NMR peaks are complex multiplets or broad [ppm (relative integral)]: ^{1}H NMR (CDCl$_3$) δ 7.46, 7.38, 7.33 (2H), 0.95 (0.85H), 0.64 (2.20H), 0.32 (2.92H); ^{13}C NMR (CDCl$_3$) δ 138.1, 136.6, 135.2, 0.62, 0.24, 0.15; ^{29}Si{^{1}H} δ −6.63, −15.61, −25.54 (the fourth peak corresponding to completely thiophene-substituted Si was not visible due to excessive baseline noise). Anal. Calcd for C$_6$H$_8$SiS: C, 51.38; H, 5.75. Found: C, 51.62; H, 5.56.

Synthesis of Hyperbranched Polymer 3b. A 100-mL, three-necked round-bottomed flask was charged with magnesium turnings (2.43 g, 0.100 g atom). The magnesium was dry-stirred for 2 h, and then THF (5 mL) was added. A solution of vinyl bromide (11.8 g, 110 mmol) in THF (20 mL) was added dropwise. After completion of addition, additional THF (50 mL) was added and the mixture was stirred at room temperature for 2 h. To this Grignard solution was added a solution of **2**, which was prepared from 7.38 g (26.1 mmol) of **1**. The resulting mixture was stirred at room temperature for 1 day. Methanol (20 mL) was added to react with excessive Grignard reagent. Most of the volatiles were removed under reduced pressure, and 500 mL of hexane was added to the residue. The suspension was filtered, and all volatiles were removed under reduced pressure to yield the crude product as a yellow-orange sticky semisolid. The crude product was purified by dissolving in chloroform and precipitating into a large excess of methanol chilled in a dry ice/acetone bath. Polymer **3b** was obtained as a yellow-orange sticky solid in 69% yield (2.96 g). $T_g = 14$ °C. Molecular weight: M_n 6587, M_w 67 535 (GPC, polydispersity: 10.3); M_n 10 480 (VPO). All NMR peaks are complex multiplets or broad [ppm (relative integral)]: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.55−7.41 (2H), 6.59−6.21 (4H), 5.93−5.84 (2H); ^{29}Si{^{1}H} δ −29.1, −31.2, −33.4, −35.7. Anal. Calcd for C$_8$H$_8$SiS: C, 58.48; H, 4.91. Found: C, 58.23; H, 5.04.

Synthesis of Hyperbranched Polymer 3c. A 100 mL three-necked round-bottomed flask was charged with magnesium turnings (2.43 g, 0.100 mol). The magnesium was dry-stirred for 2 h, and then THF (10 mL) was added. 2-Bromo-

thiophene (14.9 g, 91 mmol) was added dropwise. After completion of addition, additional THF (50 mL) was added and the mixture was stirred at room temperature for 2 h. To this Grignard solution was added a solution of **2** which was prepared from 6.38 g (22.5 mmol) of **1**. The resulting mixture was heated to 90 °C in an oil bath for 2 days. Methanol (10 mL) was added to react with excessive Grignard reagent, and the mixture was filtered. The filtrate was added to a large excess of methanol, resulting in the formation of a white precipitate. The precipitate was collected, washed with methanol, and dried under vacuum to give **3c** in 76% yield (4.73 g). $T_g = 120$ °C. Molecular weight: M_n 5481, M_w 14 900 (GPC, polydispersity 2.7); M_n 10125 (VPO). All NMR peaks are complex multiplets or broad [ppm (relative integral)]: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42, 7.09; ^{29}Si{^{1}H} δ −34.5, −34.8, −35.6 (the peak for the completely substituted silicon atoms is expected to be buried in this region). Anal. Calcd for C$_{12}$H$_8$-SiS$_3$: C, 52.14; H, 2.92. Found: C, 51.68; H, 2.85.

Synthesis of Hyperbranched Polymer 3d. A 100 mL three-necked round-bottomed flask was charged with magnesium turnings (2.43 g, 0.100 mol). The magnesium was dry-stirred for 2 h, and then THF (10 mL) was added. Bromobenzene (15.7 g, 100 mmol) was added dropwise. After completion of addition, additional THF (50 mL) was added and the mixture was stirred at room temperature for 3 h. To this Grignard solution was added a solution of **2**, which was prepared from 6.76 g (23.9 mmol) of **1**. The resulting mixture was heated to 90 °C in an oil bath for 2 days. Methanol (10 mL) was added to react with excessive Grignard reagent, and the mixture was filtered. The filtrate was added to a large excess of methanol, resulting in the formation of a white precipitate. The precipitate was collected, washed with methanol, and dried under vacuum to give **3d** in 86% yield (5.46 g). $T_g = 135$ °C. Molecular weight: M_n 5425, M_w 16166 (GPC, polydispersity 3.0); M_n 9216 (VPO). All NMR peaks are complex multiplets or broad [ppm (relative integral)]: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.51−7.19; ^{29}Si{^{1}H} δ −19.1, −24.5, −30.0, −35.6. Anal. Calcd for C$_{16}$H$_{12}$SiS: C, 72.68; H, 4.57. Found: C, 72.44; H, 4.60.