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# Electroactive and Conducting Star-Branched Poly(3-hexylthiophene)s with a Conjugated Core

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Received November 17, 1998; Revised Manuscript Received April 27, 1999

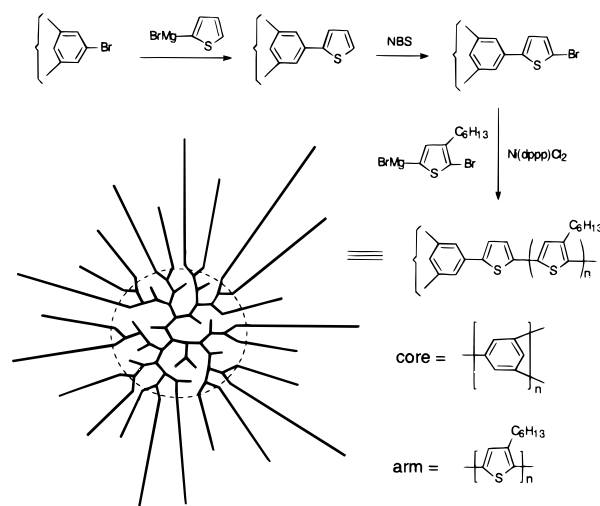
**ABSTRACT:** A new star structured regioregular poly(3-hexylthiophene) with a conjugated hyperbranched poly(triphenylamine) as the core has been shown to be electroactive and able to attain high levels of conduction up to 100 S/cm when doped. A hyperbranched poly(triphenylamine) was synthesized by a Negishi coupling reaction from tris(4-bromophenyl)amine with the terminal bromo group on the hyperbranched polymer subsequently converted to a bromothiophene. This functionalized hyperbranched polymer was used as a core for the synthesis of a star structured regioregular poly(3-hexylthiophene). The star polymer has a fully conjugated system with conjugated arms of poly(3-hexylthiophene) attached to a conjugated core of poly(triphenylamine). The solution, optical, and thermal properties of the polymers were investigated by SEC, UV–vis spectroscopy, TGA, and DSC. The results indicated that with the branched star structure the polymer retained a high degree of structural order as is typical for regioregular poly(3-alkylthiophene)s.

## Introduction

Electronically conductive polymers are typically composed of linear conjugated systems, exemplified by the breadth of work published on polyacetylene, polypyrrole, polyaniline, polythiophene, and other polymers.<sup>1</sup> Structural homogeneity and solid-state packing play important roles in determining the properties of conducting polymers.<sup>2</sup> For example, highly regioregular poly(3-alkylthiophene)s have been reported in which the 3-alkylthiophene rings are connected in a uniform head-to-tail fashion.<sup>3,4</sup> Thin films cast from these regioregular polymers can self-assemble to give highly ordered crystalline domains. X-ray evidence suggests that these domains consist of organized poly(3-alkylthiophene) sheets which assemble into laminar stacks.<sup>5</sup> Such unique self-assembly properties derive from the supramolecular structures that exist in the regioregular poly(3-alkylthiophene) solutions.<sup>6</sup> Their electrical conductivity in the solid state after doping is significantly higher than films made with regiorregular polymers and is related to intermolecular charge transport between planes.<sup>3,4</sup> Generally speaking, such highly ordered systems produce two-dimensional anisotropy. There have been some efforts directed toward the study of three-dimensional systems of conducting polymers. For example, fully conjugated conducting gels made from poly(3-octylthiophene) with conjugated cross-linking reagents have been synthesized and studied.<sup>7</sup>

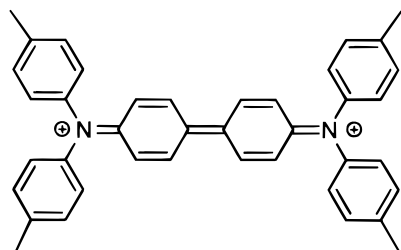
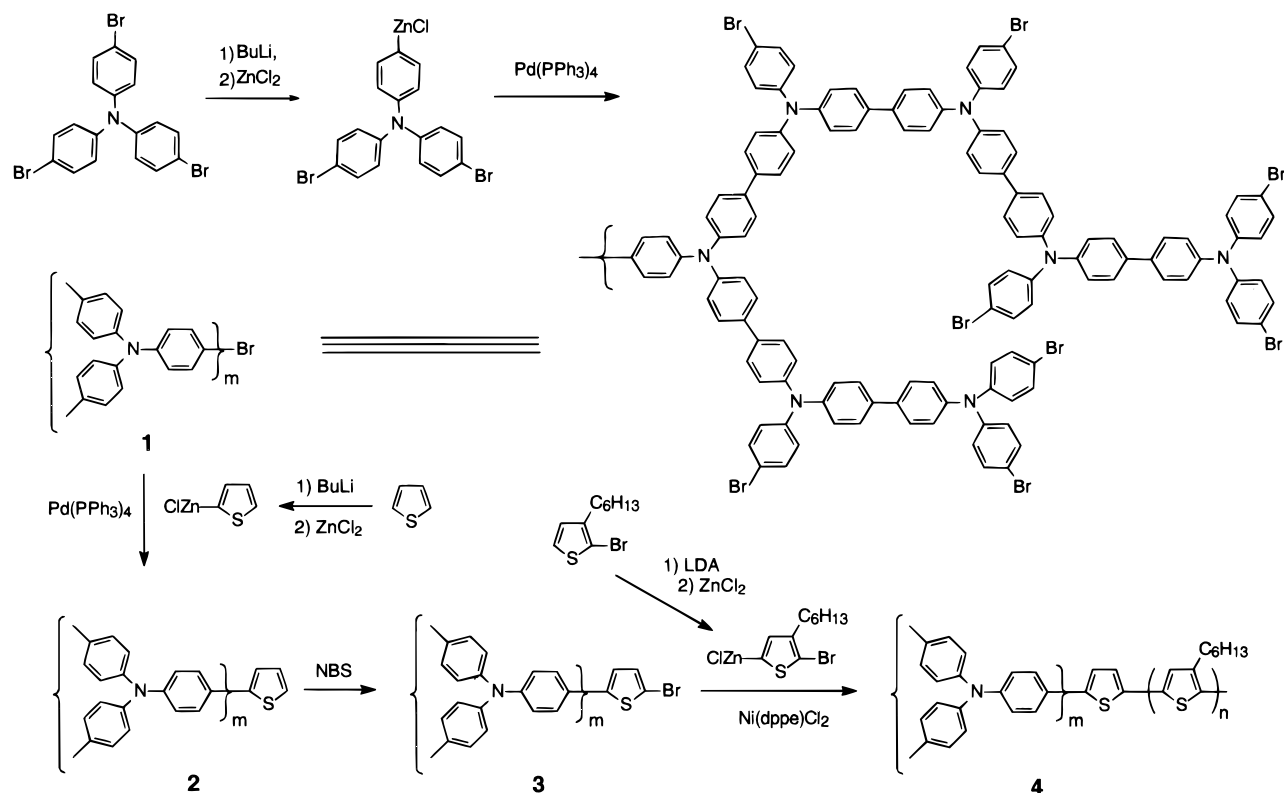
Hyperbranched polymers with conjugated systems have been reported with the goal of developing three-dimensional structures.<sup>8</sup> Specifically, poly(amidoamine) dendrimers have been peripherally modified with anion radical moieties to generate electrically conducting dendrimers.<sup>9</sup> The films cast from these dendrimers are electronically conductive and isotropic, demonstrating the three-dimensional nature of the charge transport.

Scheme 1



Star polymers are a class of branched macromolecules which typically consist of a number of linear polymer arms joined together by a central core.<sup>10</sup> To provide further insights into the effect of conducting polymer structure on solid-state properties, we prepared and characterized an electrically conducting polymer with a star structure.<sup>11</sup> In this instance, the core of the star was an electroinactive hyperbranched poly(1,3,5-phenylene) with regioregular poly(3-hexylthiophene) (P3HT) conducting arms radiating from the core as illustrated by Scheme 1. The results show that, even with the restricted and branched structure, the star polymer with P3HT arms can self-assemble into thin films with morphological, electrical, and optical properties that reveal a surprisingly high degree of structural order. The polyphenylene core used for that star polymer synthesis was not a conjugated system due to the 1,3,5-substitution pattern which prohibits the core from

### Scheme 2



**Figure 1.** Structure of the hyperbranched poly(triphenylamine) core indicating the dicationic conjugated unit.

becoming conductive upon doping. In this system, charge carriers are delocalized along the polymer arm chains, with hopping between the arms to yield a conducting material.

Here we report on a new conducting star polymer using a combination of a conjugated core and conjugated arms which, after doping, yield a fully conducting star structure. The conductive pathway can therefore go through both the core and the arms; thus, a much larger conjugated system is expected along with a truly three-dimensional conducting material. A recent report presented a hyperbranched conjugated polymer containing a triphenylamine structure.<sup>12</sup> The polymer was prepared using an AB<sub>2</sub>-type monomer via the coupling of bis(4-bromophenyl)-4'-bromomagnesium phenylamine by a Grignard reaction to form a hyperbranched poly(triphenylamine). The structural difference between this polymer and the poly(1,3,5-phenylene) is that the branching point in this case is nitrogen, which can participate in the formation of a charge-stabilizing conjugated structure upon oxidation as shown in Figure 1. Such a structure allows the conjugation from the biphenyl to continue through the nitrogen, and a fully conjugated hyperbranched structure can be obtained. In work reported here, the core in the star is composed of a

hyperbranched poly(triphenylamine) while the arms are regioregular poly(3-hexylthiophene).

## Results and Discussion

**Synthesis.** Our initial efforts to synthesize the poly(triphenylamine) were conducted following a reported method.<sup>12</sup> However, the Grignard reaction did not give satisfactory results, with the major product being an insoluble material, while only a small fraction of low molecular weight soluble poly(triphenylamine) was obtained. Therefore, a different approach was undertaken. The Negishi coupling reaction was used for the synthesis of hyperbranched poly(triphenylamine) and its capping with thiophene (Scheme 2). Tris(4-bromophenyl)amine was monolithiated by *n*-BuLi at  $-78^{\circ}\text{C}$  in THF with slightly less than 1 equiv of *n*-BuLi. (Any excess tris(4-bromophenyl)amine will not interfere with polymerization but can contribute as a core for polymer formation. Also, the *n*-BuLi was added to the reaction solution slowly to avoid dilithiation. Such a dilithiated species could produce a cross-linking reaction.) The lithiated species was then reacted with  $\text{ZnCl}_2$  to give the chlorozinc species. Polymerization was initiated by the addition of  $\text{Pd}(\text{PPh}_3)_4$  (tetrakis(triphenylphosphine)palladium) followed by refluxing overnight. The resulting polymer **1** was fully soluble in THF and was recovered by precipitation into methanol.

To cap **1** with thiophene, lithiation of thiophene by *n*-BuLi at  $-78^{\circ}\text{C}$  in THF was followed by reaction with  $\text{ZnCl}_2$  to generate the 2-chlorozinciothiophene. Coupling of the 2-chlorozinciothiophene with **1** by  $\text{Pd}(\text{PPh}_3)_4$  produced polymer **2**, which was subsequently brominated with NBS using an established procedure<sup>11</sup> giving polymer **3** in high yield. In this instance, the reaction medium for bromination was a mixture of chloroform, acetic acid, and carbon disulfide. Acetic acid is a nonsolvent for polymer **2**, and to keep the polymer in

Table 1. SEC Results for Polymers 1–4 and L-P3HT

	$M_w$	$M_w/M_n$	$[\eta]$ (dL/g)
<b>1</b>	5100	1.83	0.035
<b>2</b>	5100	1.42	0.053
<b>3</b>	6800	1.56	0.049
<b>4</b>	24400	1.57	0.23
L-P3HT	25900	1.60	0.28

solution, a very good solvent for **2**, carbon disulfide, was required for a homogeneous reaction.

The synthesis of star-branched regioregular P3HT **4** with polymer **3** as the core was conducted using Negishi coupling conditions. To ensure that regioregular P3HT could be prepared using the Negishi reaction, we synthesized 2-bromo-5-chlorozincio-3-hexylthiophene by lithiation of 2-bromo-3-hexylthiophene with LDA (lithium diisopropylamide) followed by reaction with  $\text{ZnCl}_2$ . When this monomer was polymerized using  $\text{Pd}(\text{PPh}_3)_4$ , a regiorandom P3HT was obtained as evidenced by the visible spectrum. This is consistent with the report that 2-bromo-5-bromozincio-3-hexylthiophene yielded a regiorandom polymer when polymerized with this catalyst.<sup>4</sup> On the other hand, when 2-bromo-5-chlorozincio-3-hexylthiophene was polymerized using  $\text{Ni}(\text{dppe})\text{Cl}_2$  ([1,2-bis(diphenylphosphino)ethane]nickel(II) chloride), a regioregular P3HT was obtained as evidenced by the visible spectrum. Therefore, to obtain regioregular arms in the star polymer, polymerization of **4** was carried out using  $\text{Ni}(\text{dppe})\text{Cl}_2$  as catalyst. Polymer **4** was isolated as a dark purple solid similar to the star polymer obtained when the hyperbranched polyphenylene was used as a core.

**Characterization and Properties.** The molecular weights of the polymers were determined by size exclusion chromatography (SEC) equipped with an on-line light-scattering detector, viscometer, and refractive index detector. The combination of the three detectors can provide information on the hydrodynamic volume, absolute molecular weight, and intrinsic viscosity and can generate Mark–Houwink results. As evident in the SEC results summarized in Table 1, the molecular weight changes from polymers **1** to **3** are consistent with the structural changes. As expected, comparing **1** to **2** (replacement of bromine by thiophene), there is almost no gain in molecular weight, while changing from **2** to **3** reflects the addition of bromine. The intrinsic viscosities of polymers **1**, **2**, and **3** are low, consistent with their hyperbranched structure. These results indicate polymer **1** to contain about 16 repeat units on average, and as the following two reaction steps are almost quantitative, polymer **3** contains approximately 16 bromothiophene functional groups per molecule. It is estimated that the number of arms in each star **4** is about 10–15 as reaction is not expected to be quantitative. Using the molecular weight differences, one can calculate the average degree of polymerization for the P3HT arms to be about 10. A linear regioregular poly(3-hexylthiophene) was purchased from Aldrich and used as the linear analogue for SEC characterization. The SEC of **4** and the linear P3HT (L-P3HT) are shown in Figure 2. It can be seen that, while the molecular weights of these two polymers are quite similar, the star polymer has a larger retention volume, indicating a smaller hydrodynamic size. The intrinsic viscosity of the star polymer is also smaller and is an indication of the star structure proposed. Further evidence for star formation of polymer **4** is demonstrated in the Mark–Houwink plot shown in Figure 3. It has been demon-

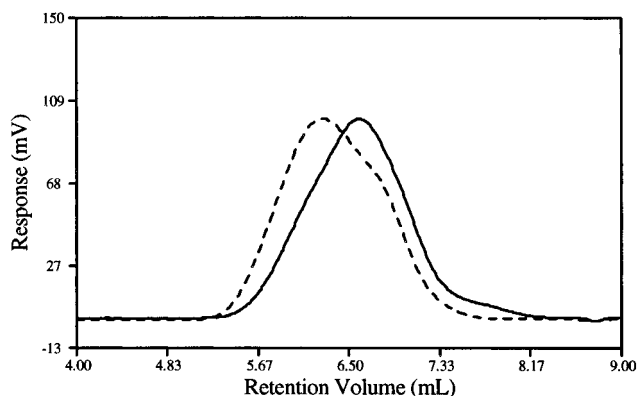


Figure 2. SEC chromatograms of star P3HT **4** (solid line) and L-P3HT (dashed line).

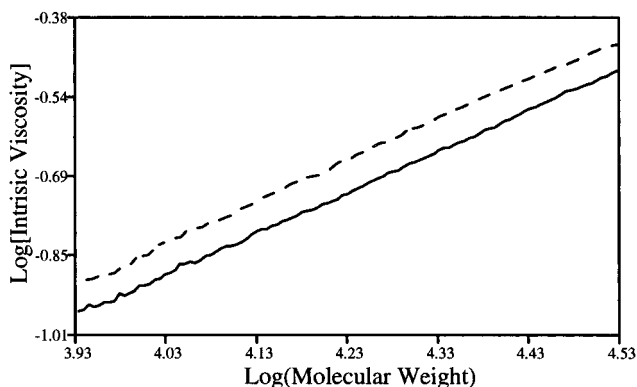
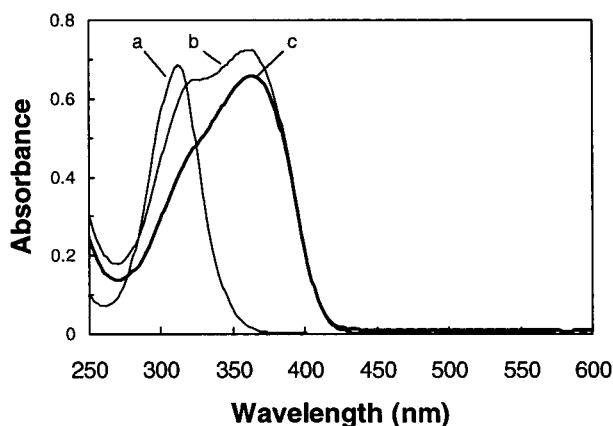


Figure 3. Mark–Houwink plot for star P3HT **4** (solid line) and L-P3HT (dashed line).

strated, in making comparisons of linear and star polybutadienes, that the slopes of the lines from the star polymers are the same as the slope for the linear polymers. At the same time, the intercepts of the lines decrease with an increase in the number of arms in the star polymers.<sup>13</sup> As polymer **4** has a smaller intercept value than the L-P3HT, these characterization results further confirm that the star polymer made by the Negishi coupling reaction has the desired branched, more compact structure.

To understand the molecular structure of the P3HT-based star polymers,  $^1\text{H}$  NMR and FT-IR studies were carried out. The  $^1\text{H}$  NMR spectrum of **1** shows a complex set of multiple peaks in the aromatic range from 6.8 to 7.6 ppm. The IR spectrum of **1** shows, as expected, that the  $510\text{ cm}^{-1}$  band due to the C–Br stretching vibration is reduced in intensity compared to that of monomer (since most C–Br bonds are consumed in core formation). The remaining C–Br bonds in the polymer are those on the periphery and available for appending the arms. In addition, a new band at  $1599\text{ cm}^{-1}$  supports the formation of C–C bonds between aromatic rings. The  $^1\text{H}$  NMR spectrum of **2** shows a group of peaks with maxima centered around 7.19 ppm that are due to the thieryl protons. Because these peaks overlap with the other aromatic peaks, integration cannot be used to determine the substitution level. In the IR spectrum of **2**, the  $510\text{ cm}^{-1}$  band of the C–Br bond has disappeared completely, and a new band at  $693\text{ cm}^{-1}$  due to the thiophene rings appears. Elemental analysis of **2** showed a near expected sulfur-to-nitrogen ratio, indicating an almost full level of substitution. In the  $^1\text{H}$  NMR spectrum of **3**, the intensity of the peaks due to thiophene protons decreased, and elemental analysis showed one



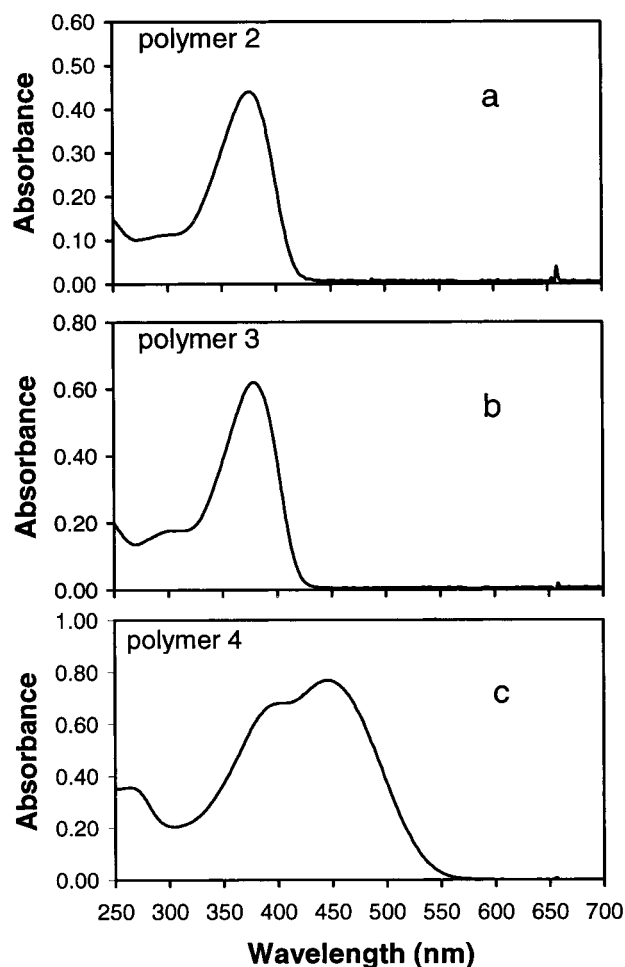
**Figure 4.** Solution UV-vis spectra of (a) tris(4-bromophenyl)amine, (b) low molecular weight type **1** polymer made by Grignard method, and (c) core polymer **1** (all in chloroform).

bromine for each sulfur, as expected. The  $^1\text{H}$  NMR spectrum of **4** showed both the typical peaks from regioregular P3HT as well as broad aromatic peaks assignable to the protons in the poly(triphenylamine) core. Elemental analysis showed some bromine in the sample, which is likely due to the terminal bromines on the thiophene chains.

The solution UV-vis spectra of the starting material, tris(4-bromophenyl)amine, core polymer **1**, and a low molecular weight core type polymer **1** made using a Grignard method are shown in Figure 4 for comparison. It can be seen that the monomer has a band with  $\lambda_{\text{max}} = 310$  nm, which is assignable to the aniline-like absorption. Polymer **1** has its major absorbance band at  $\lambda_{\text{max}} = 360$  nm where the lower energy  $\pi-\pi^*$  transition indicates the increased conjugation in the diamine-biphenyl system. There is a large shoulder at 322 nm in the low molecular weight **1**, which is due to the terminal bromophenyl units. The intensity of this shoulder is reduced in the higher molecular weight **1** due to the lower content of peripheral reactive groups. The solution and solid-state UV-vis spectra data are summarized in Table 2.

The solution UV-vis spectra of polymers **2**, **3**, and **4** are shown in Figure 5. It can be seen in the spectrum of **2** that the 322 nm shoulder has, as expected, disappeared completely, while the  $\lambda_{\text{max}}$  red-shifted from 362 to 376 nm. This shift to a lower energy transition indicates that the conjugation length has increased with addition of the terminal thiophene. Bromination of this terminal thiophene has little effect on the UV-vis spectra as the  $\lambda_{\text{max}}$  for **3** is only shifted slightly to 378 nm. In the spectrum of polymer **4**, the  $\pi-\pi^*$  energy transition from the core appears as a shoulder, and the transition for the P3HT arms in the star structure is the same as for the linear P3HT with  $\lambda_{\text{max}}$  at 446 nm.

The solid-state UV-vis spectra of polymers **1–4** are shown in Figure 6. Similar to its solution spectra, the solid-state spectrum of **1** has a shoulder due to the terminal units which are not visible in polymer **2**. Polymers **2** and **3** have almost identical solid-state spectra, and the  $\lambda_{\text{max}}$  of **1** to **3** are at essentially the same energies in both solution and solid. The solid-state spectrum of **4** shown in Figure 6d has the expected low-energy  $\pi$  to  $\pi^*$  transition due to the regioregular P3HT arms. An interesting phenomenon is observed when comparing the relative intensities due to the core and the arms in solution and the solid state. In the solution, as evident in Figure 5c, the two absorbances are of

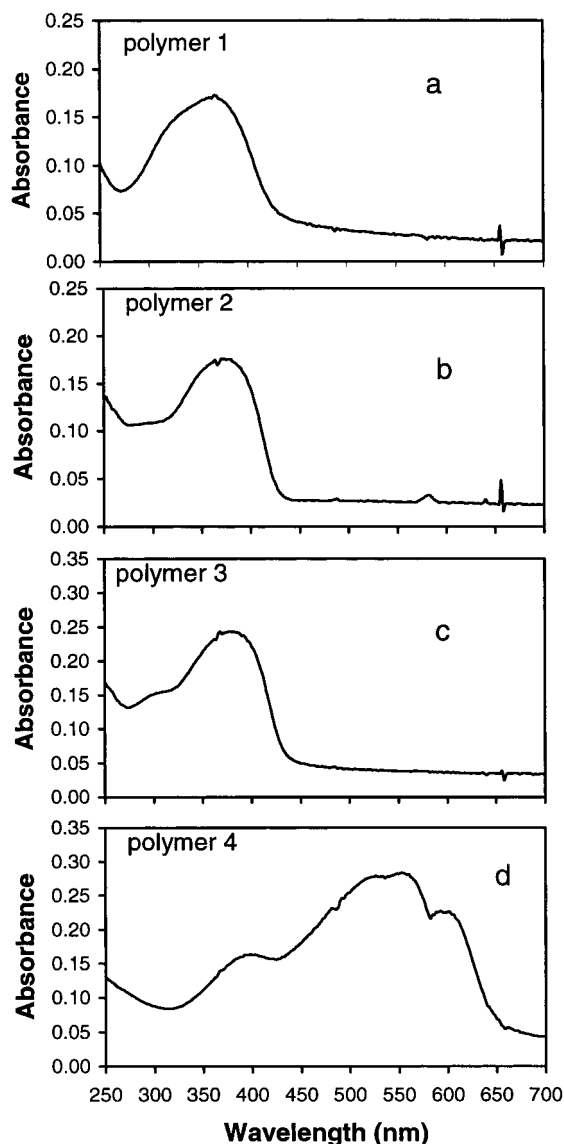


**Figure 5.** Solution UV-vis spectra of (a) polymer **2**, (b) polymer **3**, and (c) polymer **4**.

similar intensities. Considering the relatively small fraction of the core relative to the arm in the star polymer, this suggests that the core has a higher molar absorptivity. Examination of the spectrum taken of the solid (Figure 6d) shows a red-shifting of the absorbance due to the P3HT arms and a simultaneous increase in the arm-to-core ratio in absorbance intensity. These changes can be attributed to an increase in the conjugation length of the conjugated regioregular thiophene chains in the solid as torsional defects present in solution are eliminated. This does not occur with the poly(triphenylamine) core as the chromophores are of a discrete length and are less sensitive to conformation.

The thermal properties of these polymers were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) and are summarized in Table 3. TGA was conducted under nitrogen, and the thermograms for polymers **1–4** are shown in Figure 7. It can be seen that all the polymers are quite thermally stable up to 300 °C. Polymer **1** began to lose weight at temperatures over 350 °C with a weight loss during the first stage of about 25% corresponding to the weight percent of bromine in the sample. There is a high char level retained up to 900 °C due to the fully aromatic structure in the polymer. The fully aromatic polymer **2** is very thermally stable with substantial weight loss beginning at temperatures over 550 °C. Polymer **3** has a TGA thermogram similar to **1**, nicely complementing the results which suggest Br extrusion. Polymer **4** contains aliphatic side chains, and thermal decomposition is believed to begin with their decomposition





**Figure 6.** Solid-state UV-vis spectra of (a) polymer 1, (b) polymer 2, (c) polymer 3, and (d) polymer 4.

**Table 2.** UV-vis Data of Polymers 1-4

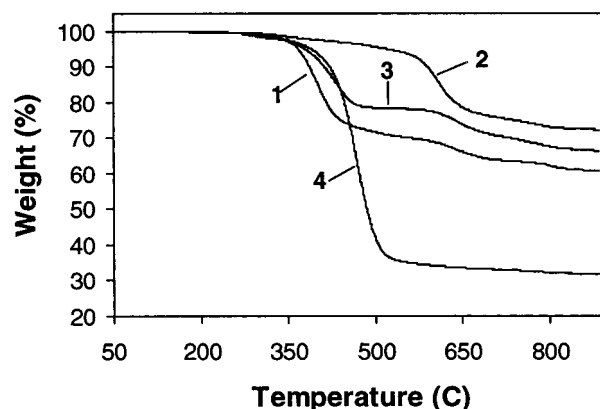
	$\lambda_{\text{max}}$ (nm)	
	solution	solid
1	362	366
2	376	374
3	378	378
4	404, 446	400, 526, 552, 592

**Table 3.** TGA and DSC Results for Polymers 1-4

	$T_{\text{od}}^a$ (°C)	$T_g$ (°C)	$T_m$ (°C)
1	389	193	
2	593	203	
3	392	197	
4	434		231

<sup>a</sup>  $T_{\text{od}}$  = onset of decomposition temperature.

followed by the linear polymer. The glass transition temperatures of these polymers were determined by DSC. All of the hyperbranched polymers have similar  $T_g$ 's around 200 °C. It should be noted that this behavior is different from the thermal study conducted on functionalized hyperbranched poly(1,3,5-phenylene)s where chain ends are found to have a large effect on thermal

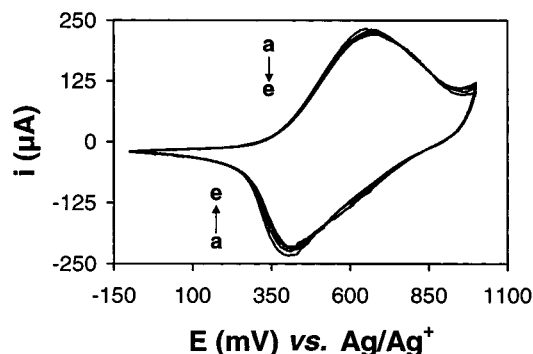


**Figure 7.** TGA thermograms for polymers 1-4 in  $N_2$  at a scan rate of 20 °C/min.

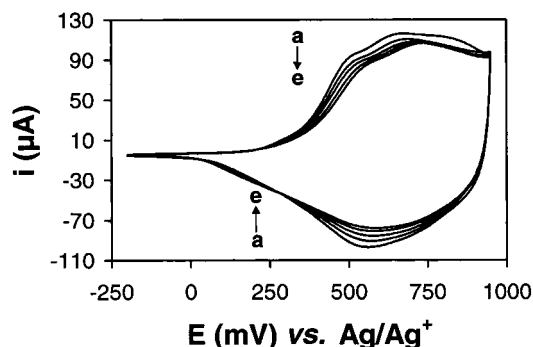
relaxations.<sup>14</sup> We believe such different thermal behavior is due to structural differences. In polyphenylene, the branching points are close to one another with every neighboring phenylene being a branching point. The polymer is a highly compact spherulike structure, and therefore the chain end has a very large effect on the thermal relaxation of the polymer. The poly(triphenylamine) has a relatively long spacer between each branching point and therefore forms a more open structure. The thermal relaxation behavior for this type of polymer is more dependent on the overall structure and less on the chain ends. There is no  $T_g$  observed for polymer 4, similar to the star polymer made from a polyphenylene core.<sup>11</sup> A melting transition was observed for 4, indicating that the polymer has a highly crystalline structure and the  $T_m$  is very similar to the  $T_m$  observed for the star polymer with polyphenylene core. As polymer 4 is composed mainly of regioregular poly-(3-hexylthiophene), its thermal behavior is dominated by this material.

The conductivities for the iodine-doped polymer films were measured by a four-point probe technique. Low conductivities of about 0.01 S/cm were found for doped polymer 2 as expected. The conductivities for polymer 4 were significantly higher, 70–100 S/cm, similar to the value reported for the star P3HT polymer with polyphenylene as the core (65 S/cm).<sup>11</sup> As such, the high conductivity in the star polymers is mainly due to the regioregular P3HT arms. Further detailed studies on the conductivity will reveal whether the expected three-dimensional structure of these polymers exists and plays a role in their properties.

The electrochemical response of polymers 2 and 4 was studied by cyclic voltammetry in acetonitrile, using Ag/Ag<sup>+</sup> as a reference electrode. As the poly(triphenylamine) core capped with a thiophene (polymer 2) is conjugated, it is electroactive. Therefore, a reversible redox process was observed upon cycling, with an  $E_{1/2}$  at about +0.5 V as shown in Figure 8. Note that this redox process only involves a single redox system because only one oxidation and one reduction peak appear in the cyclic voltammogram. A relatively high stability of polymer 2 upon cycling was also noticed since no significant decrease of the peak intensities was recorded after 50 cycles between -0.1 and +1.0 V (see Figure 8). As polymer 4 contains an electroactive core (polymer 2) and linear P3HT arms, two different redox processes were expected in the cyclic voltammograms of this star polymer. Figure 9 clearly shows two oxidation peaks and a broad reduction peak. The first



**Figure 8.** Cyclic voltammograms of polymer **2** as a function of repeated scans: (a) scan 10, (b) scan 20, (c) scan 30, (d) scan 40, and (e) scan 50.



**Figure 9.** Cyclic voltammograms of polymer **4** as a function of repeated scans: (a) scan 10, (b) scan 20, (c) scan 30, (d) scan 40, and (e) scan 50.

oxidation peak is located at about +0.5 V and the second one at about +0.7 V. Comparing Figures 8 and 9, the first redox process likely corresponds to the P3HT arms and the second to the core. Note that no noticeable change appears in the cyclic voltammogram between cycles 20 and 50 (see Figure 9). This underlines the good stability of the star polymer upon cycling. Even though polymer **4** is mainly composed of regioregular P3HT, its electrochemical behavior seems to be a combination of the response of the electroactive core and the P3HT arms. Examining the influence of arm length on the electrochemical response will certainly provide a better understanding of the redox system observed in the cyclic voltammograms of these conjugated star polymers. An extensive electrochemical and spectroelectrochemical study of different conjugated star polymers is currently under way.

In summary, we have successfully developed a synthetic method for hyperbranched, conjugated poly(triphenylamine) and its functionalization with bromothiophene. A regioregular P3HT star structured polymer has been synthesized from the conjugated core. The branched star structure was confirmed by SEC characterization. The solid-state UV-vis spectrum of the star polymer showed low-energy transitions typical for the regioregular structure of poly(3-alkylthiophene)s. The star polymer can be doped to high levels of conductivity and is redox electroactive.

## Experimental Section

**General.** All reagents and solvents were used as purchased from Aldrich Chemical.  $^1\text{H}$  NMR spectra were recorded on a Hitachi R-1500 FT-NMR spectrometer at 60 MHz. Infrared spectra were recorded on a Nicolet 750 FTIR spectrometer. UV-vis spectra were recorded on a HP 8452A UV-vis diode

array spectrophotometer. Solid-state UV-vis spectra were obtained by casting a thin film from chloroform solution of polymers onto quartz substrates. Size exclusion chromatography was conducted on a Hewlett-Packard series 1050 HPLC with a Hewlett-Packard 1047A refractive index detector and a Viscotek T60 light scattering and viscosity detector; data analysis was done by Viscotek Trisec GPC software version 3.0. One Polymer Laboratories PL gel  $5\mu$  mixed-D column was used with THF as solvent. TGA was conducted on a Perkin-Elmer TGA7 thermogravimetric analyzer under nitrogen with a heating rate of  $20^\circ\text{C}/\text{min}$ . DSC was conducted on a Perkin-Elmer DSC7 differential scanning calorimeter under nitrogen with a heating rate of  $10^\circ\text{C}/\text{min}$ . All samples were heated to  $250^\circ\text{C}$  and quenched in liquid nitrogen before DSC measurement. Elemental analyses were accomplished at Galbraith Laboratories, Inc.

Cyclic voltammetry was carried out with an EG&G Princeton Applied Research model 273 potentiostat/galvanostat employing a gold button working electrode (diameter 1.6 mm), a platinum plate counter electrode, and an  $\text{Ag}/\text{Ag}^+$  reference electrode. The electrolyte used was 0.1 M lithium perchlorate in acetonitrile. The scan rate was set to  $20\text{ mV/s}$  using the EG&G M270 software. Polymer films were cast with a microsyringe on the surface of the working electrode from a 2% solution in chloroform. These films were allowed to dry for 2 h at room temperature prior to characterization.

**Poly(triphenylamine) (1).** In a 250 mL round-bottom flask, tris(4-bromophenyl)amine (9.64 g, 20 mmol) was dissolved in 100 mL of dry THF, and the solution was bubbled with Ar for 20 min. The solution was cooled to  $-78^\circ\text{C}$ , and butyllithium (1.6 M, 12.2 mL, 19.5 mmol) was added dropwise via a syringe over 30 min. The color of the reaction mixture changed from dark gray to dark reddish purple. After the addition was completed, the solution was stirred for 20 min at  $-78^\circ\text{C}$ . Zinc chloride in THF (0.5 M, 44 mL, 22 mmol) was added via a syringe as quickly as possible. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. A yellow solution was obtained. Tetrakis(triphenylphosphine)palladium (0.23 g, 0.2 mmol) was added into the flask, and the resulting mixture was heated to reflux overnight. The cooled solution was filtered to remove any insoluble materials and poured into 150 mL of methanol, and the polymer was precipitated as a yellow solid. The polymer was collected by filtration and washed with methanol, water, and methanol and dried in a vacuum oven overnight. A 4.96 g (77% yield) sample of polymer was obtained. The  $^1\text{H}$  NMR spectrum showed a broad multiple peak from 6.8 to 7.6 ppm. Anal. Calcd for  $(\text{C}_{18}\text{H}_{12}\text{NBr})_n$ : C, 67.10; H, 3.75; N, 4.35; Br, 24.8. Obsd: C, 63.40; H, 3.85; N, 4.09; Br, 26.61.

**Thiophene-Capped Poly(triphenylamine) (2).** Thiophene (1.18 g, 14 mmol) was dissolved in 50 mL of THF and cooled to  $-78^\circ\text{C}$ . Butyllithium (1.6 M, 7.5 mL, 12 mmol) was added dropwise via a syringe, and the reaction mixture was stirred at  $-78^\circ\text{C}$  for 15 min and then warmed to  $-10^\circ\text{C}$  and stirred for 5 min. The mixture was again cooled to  $-78^\circ\text{C}$ , and zinc chloride in THF (0.5 M, 26 mL, 13 mmol) was added via a syringe as quickly as possible. The reaction mixture was allowed to warm to room temperature and stirred for 1.5 h. In another flask, poly(triphenylamine) (2.0 g, 6.2 mmol) was dissolved in 50 mL of THF and transferred to the  $\text{ZnCl}_2$ -thiophene solution via a cannula. The resulting mixture was purged by Ar for 20 min, and then tetrakis(triphenylphosphine)palladium (0.14 g, 0.12 mmol) was added into the flask. The mixture was heated to reflux for 4 h. There was some insoluble solid formed during the reaction, and this solid was removed by filtration. The polymer was recovered and purified by precipitation in methanol and washed by water and methanol. After drying in a vacuum oven, 1.34 g (67%) of product was obtained. Anal. Calcd for (assuming 100% thiophene substitution)  $(\text{C}_{22}\text{H}_{15}\text{NS})_n$ : C, 81.20; H, 4.65; N, 4.30; Br, 0; S, 9.85. Obsd: C, 78.93; H, 4.72; N, 4.02; Br, 1.96; S, 10.24.

**Bromothiophene-Capped Poly(triphenylamine) (3).** Thiophene-capped poly(triphenylamine) (1.0 g, 3.07 mmol) was dissolved in a mixture of 15 mL of chloroform, 6 mL of carbon

disulfide, and 3 mL of acetic acid. *N*-Bromosuccinimide (0.546 g, 3.07 mmol) was added to the reaction solution in several small portions over 20 min. The resulting mixture was stirred for 1 h at room temperature. After removing the solvents, the residue was redissolved in 10 mL of THF and precipitated in methanol. The polymer was washed by methanol, water, and methanol and dried in a vacuum oven at 60 °C; 1.205 g of product was obtained for a 97% yield. Anal. Calcd for (C<sub>22</sub>H<sub>14</sub>NSBr): C, 65.35; H, 3.49; N, 3.46; Br, 19.76; S, 7.93. Obsd: C, 63.86; H, 3.53; N, 3.30; Br, 21.06; S, 8.57.

**Star Poly(3-hexylthiophene) with Conjugated Core (4).** Diisopropylamine (4.2 mL, 30 mmol) was dissolved in THF (30 mL) and cooled to -40 °C. Butyllithium (19.75 mL, 1.6 M in hexane, 30 mmol) was added dropwise and the mixture stirred at -40 °C for 40 min. The mixture was then cooled to -78 °C, and 3-hexyl-2-bromothiophene (7.42 g, 30 mmol) was added. The mixture was stirred at -40 °C for 40 min and cooled to -78 °C again, and ZnCl<sub>2</sub> (70 mL, 0.5 M in THF, 35 mmol) was added. The mixture was allowed to warm to ambient temperature with stirring over 2 h and then was added dropwise to a solution of **3** (0.4 g, 1 mmol bromo site) and Ni(dppe)Cl<sub>2</sub> (0.085 g, 0.16 mmol) in THF (50 mL) over 3 h. The mixture was stirred at ambient temperature overnight. The solution was poured into methanol and the precipitate collected by filtration. The polymer was further purified by Soxhlet extraction using methanol for 24 h and then hexane for 24 h to remove oligomers and impurities. The polymer was isolated from the remaining residue via Soxhlet extraction with chloroform. The chloroform solution was evaporated to give the title compound as a dark purple solid (2.65 g, 50%). Anal. Calcd for (C<sub>22</sub>H<sub>14</sub>NS)(C<sub>10</sub>H<sub>14</sub>S)<sub>15</sub>: C, 73.29; H, 8.01; Br, 0; S, 18.20. Obsd: C, 68.44; H, 7.52; Br, 3.21; S, 18.51.

**Acknowledgment.** Funding of this work by the U.S. Air Force AFRL/MLBP (F33615-97-C-5090) is gratefully acknowledged.

## References and Notes

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MA981781F