

An Electrically Conducting Star Polymer

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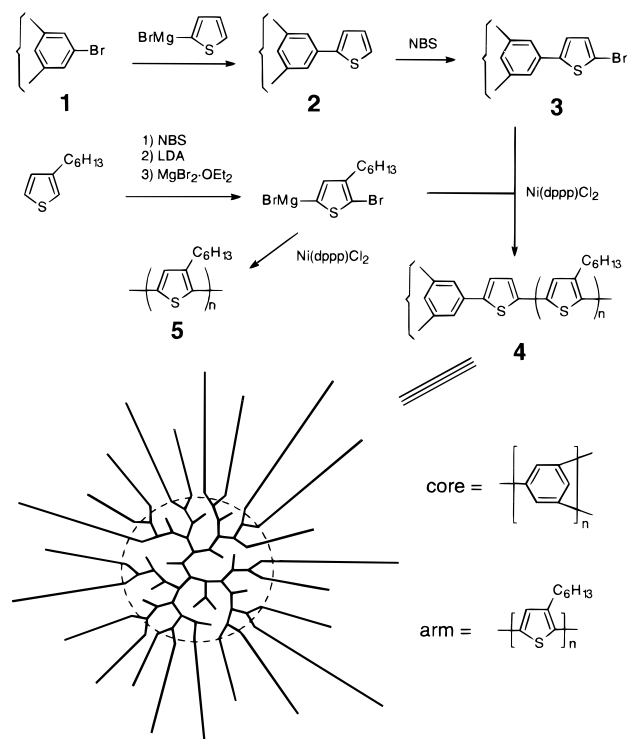
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Electronically conductive polymers typically contain as the fundamental structural unit a linear backbone of repeating conjugated monomers, exemplified by polyacetylene, polypyrrole, polyaniline, and polythiophene.¹ Structural homogeneity and solid state packing play important roles in determining the properties of conducting polymers.² For example, highly regioregular poly(3-alkylthiophenes) have been reported recently in which the 3-alkylthiophene rings are connected in a uniform head-to-tail fashion.^{3,4} Thin films cast with the regioregular poly(3-alkylthiophene)s can self-assemble to give highly ordered crystalline domains. X-ray evidence suggests that the domains consist of organized poly(3-alkylthiophene) sheets which assemble in laminar stacks.⁵ Such unique self-assembly properties derive from the supramolecular structures that exist in the regioregular poly(3-alkylthiophene) solutions.⁶ Their electrical conductivity is significantly higher than films made with the nonregioregular polymers and is related to the intermolecular charge transport within the planes.^{3,4}

To provide further insights into the effect of conductive polymer structure on solid state ordering and properties, we prepared and characterized the first example of an electrically conducting polymer with a star structure. Star polymers are a class of branched macromolecules which typically consist of a number of linear polymer arms joined together by a central core.⁷ The core of the star in this report is a hyperbranched 1,3,5-polyphenylene. Regioregular poly(3-hexylthiophene) arms (*r*PHT) radiate from the core, forming the conductive arms. The new materials constrain the polythiophene chains to point in a multiplicity of directions in the solid state. The results show that even with the constricted and branched structure, the star polymers with *r*PHT arms can self-assemble into thin films with morphological, electrical, and optical properties that reveal a surprising degree of structural order.

The synthesis of the star *r*PHT was carried out as outlined in Scheme 1 using a coupling polymerization process. The hyperbranched polyphenylene **1** was prepared according to the procedure described in the literature.⁸ The terminal bromo functional groups on the periphery of **1** have a different reactivity compared with those on the thiophene, which may affect the attachment of the polythiophene arms to the dendrimer. Therefore, the dendritic polyphenylene first was capped with bromothiophene to provide uniform branching points. This conversion was performed by coupling the polymer **1** with (bromomagnesium)thiophene to form the thiophene-capped core **2**. The thiophene substitution level was determined from the

Scheme 1



¹H NMR spectrum and elemental analysis as 52%. The conversion from **2** to **3** was conducted by bromination with *N*-bromosuccinimide (NBS). The NMR and elemental analysis results indicated that the bromination on thiophene was quantitative.

Bromination of 3-hexylthiophene on the 2-position was achieved by reaction with NBS in an acetic acid/chloroform mixed solvent which produced a high yield of the desired 2-bromo isomer.⁹ Lithiation selectively on the 5-position by lithium diisopropylamide (LDA) followed by treatment with magnesium bromide etherate gave a 2-bromo-5-(bromomagnesium)-3-hexylthiophene, which was used in the star polymer synthesis.³ The star polymer **4** was synthesized by stepwise addition of 2-bromo-5-(bromomagnesium)-3-hexylthiophene onto the core **3** in the presence of 0.5 mol % of [1,3-bis(diphenylphosphino)propane]nickel(II) chloride. This condition led to the formation of the *r*PHT star polymer **4** with 52% yield. When the polymerization was conducted without the hyperbranched core **3**, the linear *r*PHT **5** was obtained with 17% yield. The reaction conditions for these two types of polymer were very similar, so the overall molecular weight distribution of linear polymer **5** and the linear arm appendages on star polymer **4** should be similar. The low yield of the linear polymer **5** was due to the removal of the shorter thiophene polymer chains and oligomers during the purification process which involved extraction with methanol and hexane. On the other hand, the polymer and oligomer chains attached to the star were immobilized on the core and insoluble in extraction solvents, resulting in the higher yield. It is expected therefore that, in the star *r*PHT, some arms were significantly shorter than in the linear material.

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 SEC results are summarized in Table 1. The combination of the three detectors can provide information on

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Table 1. SEC Results on Polymers **1**, **4**, and **5**^a

	M_w	M_w/M_n	$[\eta]$ (dL/g)	a
1	8,900	1.85	0.03	0.31
4	37,500	2.37	0.36	0.43
5	11,100	1.28	0.12	0.73

^a M_w and M_n are the weight- and number-averaged molecular weights, η is the viscosity, and a is the exponential dependence of η on M , i.e., $\eta = KM^a$.

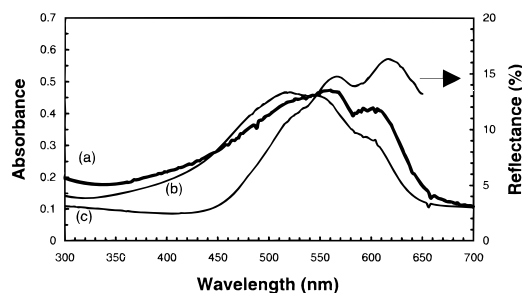


Figure 1. Solid state UV-vis spectrum of **4** (a) and **5** (b), thickness $d \approx 0.1 \mu\text{m}$; 45° specular reflectance spectrum of **4** (c), thickness $d \approx 3 \mu\text{m}$.

the absolute molecular weight and the intrinsic viscosity and also generate Mark-Houwink plots. For **5**, the exponent a in the Mark-Houwink equation was 0.73, which is within the normal range for linear polymers. For the polyphenylene core polymer **1** the value of a was only 0.31, an indication of its highly compact structure. Low a values in this range have also been observed for dendrimers.^{10,11} The Mark-Houwink plot for star polymer **4** exhibited a curved line. At the low molecular weight end of the curve, the slope was similar to that of the linear polymer while at high molecular weights the limiting slope was 0.43. It is believed that the low molecular weight star polymer contains material with a smaller core and fewer arms than the high molecular weight component. The more highly branched star polymers should be more compact. The nonlinear relationship between $\log[\eta]$ and $\log M$ has also been observed for high-generation dendrimers.¹² The polymer **1** contained about 60 phenylene rings on average as calculated from the molecular weight. The following two reaction steps generated **3** with about 30 bromothiophene functional groups per molecule. Therefore, it is estimated that the functionality in **4** is about 20 to 30. Future work will address the synthesis of star polymers and dendrimers with a more defined structure and homogenous distribution of arms.

The energies of the polythiophene π - π^* electronic transitions are qualitative indicators of the π orbital overlap in the solid state resulting from aggregation and effective conjugation length. The solid state UV-vis spectrum of films cast from **5** shows the λ_{max} at 518 nm with two shoulders at 541 and 600 nm (Figure 1). The films cast from **4**, however, show λ_{max} shifted to 558 nm, with a shoulder at ~ 530 nm and a secondary maximum at 600 nm (Figure 1). Furthermore, for films having a maximum absorbance of 0.15 to > 1 , the absorbance spectral distributions were independent of thickness for both films. This

is in basic agreement with earlier results for regioregular polyalkylthiophene films, although some thickness dependence was observed for thinner poly(3-dodecylthiophene) films in the 19–26 nm range.^{3,13} Therefore, it is believed that the shift in λ_{max} is not a thickness effect, but rather that it indicates a higher concentration of domains with more extensive π overlap in the star materials.

The surface morphologies of films cast from chloroform solutions of polymers **4** and **5** also showed very significant differences. Both films were dark purple in transmission with thick films (1–10 μm) exhibiting a golden metallic luster, while the quality of the cast film depends very much on the casting conditions.^{5,6} The films of the star polymer **4** were typically visually shiny and mirror-like, while those from the linear polymer reaction product **5** always had a diffuse scattering, rough appearance. The regioregular polythiophene either can self-assemble into highly ordered, highly conductive structure or can be disordered. The rough films cast from **5** are probably the disordered phase, or they are biphasic.^{5,6} The differences in surface morphology were examined in detail using atomic force microscopy (AFM). Films from polymer **5** displayed a rough and porous surface with larger domains (several micrometers) separated by pits ranging from 0.2 to 0.7 μm in depth. The star polymer **4** film showed a much smoother surface with smaller domains separated by pits less than 0.1 μm in depth. The root-mean-square (RMS) roughness for **4** was 20.8 nm in $50 \times 50 \mu\text{m}$ scans while the RMS roughness for **5** was 196.6 nm for the same scan area. The three-dimensional structure of the star polymer may promote a denser packing and hence a smoother surface. The specular reflectance of **4** (Figure 1) shows a pattern similar to the solid absorption spectrum obtained for thinner films but with a higher relative intensity at 616 nm.

Differential scanning calorimetry (DSC) was employed to determine the glass transition temperature T_g , crystalline melting point T_m , and crystallization point T_c of the polymers. No T_g values were observed in any of the samples. Only the T_m and T_c were observed, indicating that the rPHT polymers are highly crystalline materials. The polymer **4** had $T_m = 230 \text{ }^\circ\text{C}$ and $T_c = 183 \text{ }^\circ\text{C}$, while the values for polymer **5** were lower, $T_m = 210 \text{ }^\circ\text{C}$ and $T_c = 176 \text{ }^\circ\text{C}$. The content of the polyphenylene core in **4** is about 4%, so the different thermal properties are believed to arise from the structural differences between **4** and **5**.

The conductivities for the iodine-doped polymer films were measured by a four-point probe technique. The same magnitude level of conductivity was obtained for both polymers, typical values being 65 S/cm for **4** and 42 S/cm for **5**.

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Supporting Information Available: Details of the experimental procedure and characterization results from SEC, DSC, and X-ray diffraction (9 pages). See any current masthead page for ordering and Internet access instruction.

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