Dendrimers as Solubilizing Groups for Conducting Polymers: Preparation and Characterization of Polythiophene Functionalized Exclusively with Aliphatic Ether Convergent Dendrons

Patrick R. L. Malenfant and Jean M. J. Fréchet*

Department of Chemistry, University of California, Berkeley, California 94720-1460

Received January 3, 2000; Revised Manuscript Received March 8, 2000

ABSTRACT: The first conducting polythiophene, having only dendritic solubilizers, has been prepared using a Stille coupling approach. The use of second and third generation aliphatic ether convergent dendrons as a solubilizing platform facilitated the preparation of dendrimer-oligothiophene hybrid macromonomers having minimal substitution. Polymers were then prepared via an $A_2 + B_2$ step-growth polymerization between an oligothiophene−dibromide macromonomer and 2,5-bis(trimethylstannyl)-thiophene using $Pd(PPh_3)_2Cl_2$ as the catalyst. Both the dendrimer size and the dendrimer to thiophene unit ratio were variables that required optimization in order to obtain a solution-processable conducting polymer. Conductivities as high as 200 S/cm were measured for iodine doped thin films of the polythiophene with six thiophene repeat units for each third generation dendron.

Introduction

Since the discovery of electrical conductivity in oxidized polyacetylene,[1a] the field of conducting polymers has expanded greatly.[1] Additional technological advances in areas such as organic light emitting diodes[2] have motivated the study of several varieties of conjugated polymers. An essential characteristic of most conducting polymers is a rigid rod conjugated backbone that is able to transport charge. Unfortunately, such rigid structures are inherently insoluble, thus making it impossible to process these materials into the thin films required for most applications. Among the many conducting polymers prepared to date, polythiophenes have frequently been selected for study in numerous applications[3] due to their ease of preparation and environmental stability.[1b] As is the case for several other conducting polymers, polythiophenes must be functionalized along the main chain with solubilizing groups, such as linear alkyl side chains, to obtain soluble materials. While early poly(thiophenes) were prepared in a regio-random[4] fashion, McCullough[5] and Rieke[6] have independently demonstrated that a regioregular substitution pattern (i.e., poly(3-alkylthiophenes)) leads to materials with higher conductivities. In these systems, highly organized films result from the self-organization of the side chain solubilizers into highly ordered supramolecular structures consisting of interdigitated alkyl chains. In a different area, it has also been demonstrated that dendrimers may be used to induce the formation of highly organized structures.[7] Although there are many parameters involved in optimizing the conductivity of a material, it was felt that the combination of supramolecular ordering and the use of dendrimers as solubilizers for polythiophenes could also lead to interesting materials.

We now report our preliminary results on the use of dendrimer-oligothiophene hybrid macromonomers for the preparation of a soluble, conducting polythiophene having only dendritic substituents. Until now, dendrimers have been used mainly to isolate or shield the polymer backbone[8] and, to our knowledge, this is the first example of a conducting polymer functionalized exclusively with dendritic solubilizers. We have recently used dendrimers as solubilizers for lengthy oligothiophenes[9] as well as for the dendrimer-supported synthesis of oligothiophenes,[10] in which an aliphatic ether dendrimer was used as a solubilizing platform. Aliphatic ether dendrimers[11] are particularly attractive since they are chemically inert to the reaction conditions used to extend the oligomers (i.e., Stille coupling and *N*-bromosuccinimide (NBS) bromination reactions), thus enabling the preparation of oligothiophene macromonomers having several thiophene units and only a single solubilizing group. We anticipated that the compact structure of the aliphatic ether dendrimers should not prevent the π-stacking of the polythiophene backbones necessary for bulk charge mobility. Furthermore, it was expected that polythiophenes with minimal β-substitution might have a more planar backbone thus extending the conjugation and perhaps leading to higher conductivities.

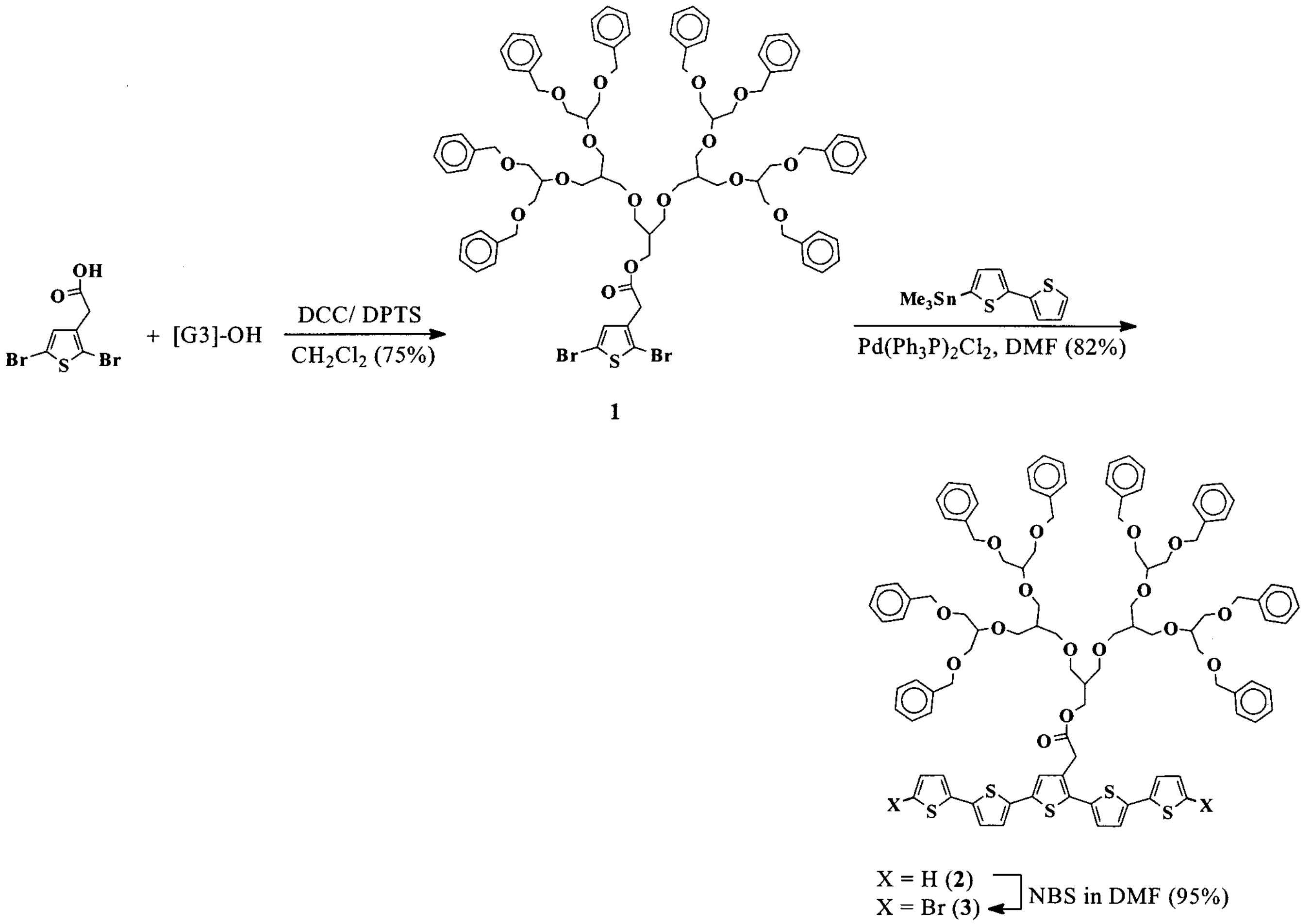
Results and Discussion

The second (G2) and third (G3) generation dendrimers were prepared according to a literature procedure.[11a] The synthesis of the G2 macromonomers has been reported previously.[10] The preparation of the G3 macromonomers is depicted in Scheme 1. The G3 monothiophene dibromide **1** was prepared by attaching 2,5-dibromo-3-thiopheneacetic acid[10] to the focal point of the dendrimer via an ester linkage using standard DCC/DPTS conditions (75%). A subsequent Stille coupling reaction between **1** and 5-(trimethylstannyl)-2,2′-bithiophene[12a] was done in DMF using $Pd(PPh_3)_2Cl_2$ as the catalyst thus providing the G3 pentamer **2** (82%). The pentamer dibromide **3** was prepared by reaction of **2** with 2 equiv of NBS in DMF (95%). The macromonomers are highly soluble in common organic solvents and were purified by flash chromatography.

Polythiophenes were prepared via an $A_2 + B_2$ polymerization protocol employing a Stille coupling reaction[13a,b] between a dendrimer bound thiophene dibromide and 2,5-bis(trimethylstannyl)thiophene[12b] (Scheme 2). Polymerizations were performed in DMF using $Pd(PPh_3)_2$-

10.1021/ma000003w CCC: $19.00

Scheme 1. Synthesis of the G3 Macromonomers

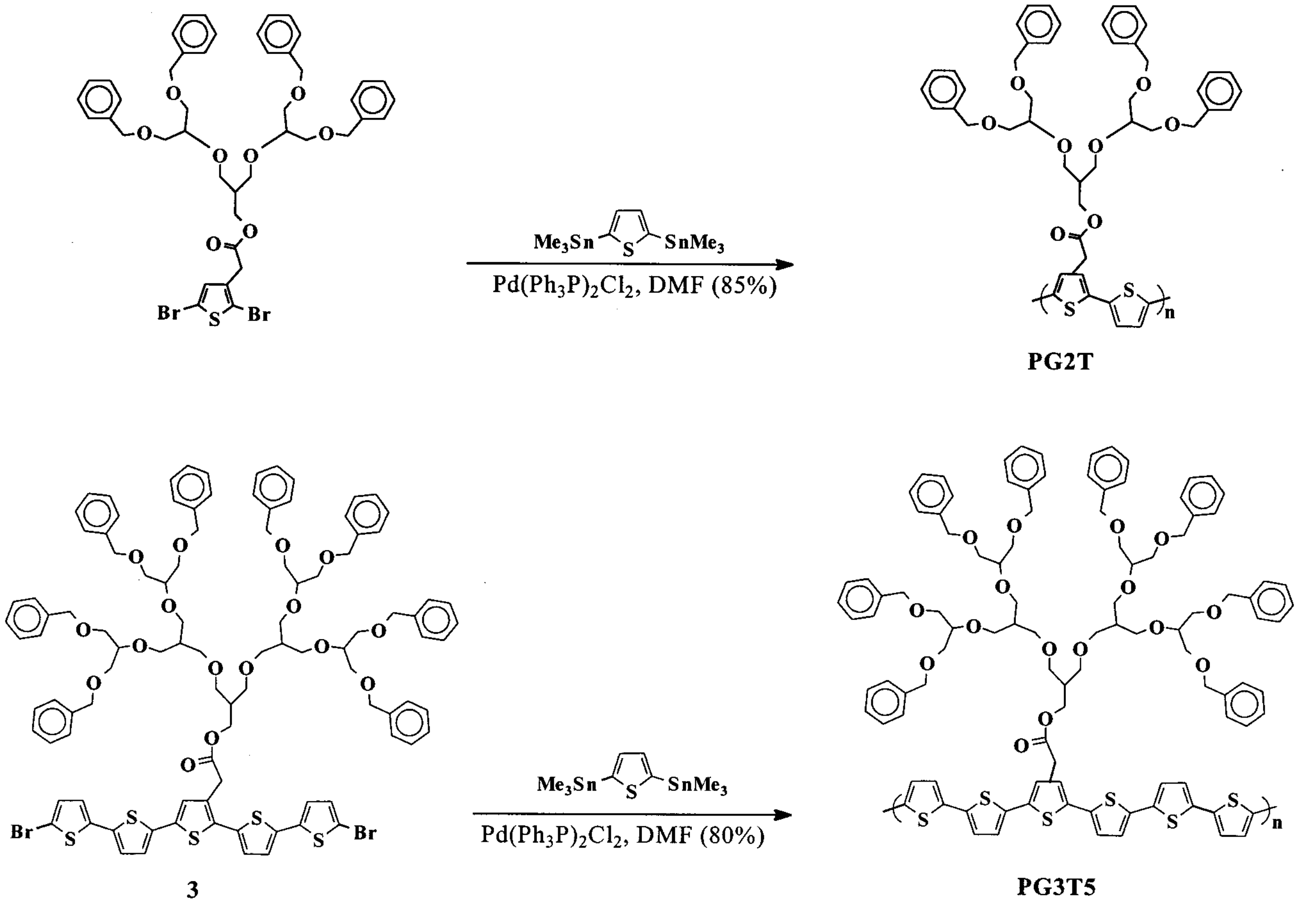


Cl_2 as the catalyst.[14] Polymerization of the G2 monothiophene dibromide **1** provided **PG2T** (85%). Although **PG2T** was found to be quite soluble in common organic solvents, it had no appreciable conductivity when doped with iodine vapor. Similar observations were made for the G3 analogue **PG3T**. The lack of charge mobility in these systems is probably due to the steric bulk of the dendrimers that precludes adequate packing of the short polymer repeat unit with one dendrimer for two thiophene units thus preventing effective charge hopping from chain to chain. Polymerization of the G2 and G3 pentamer dibromide provided **PG2T5** (94%) and **PG3T5** (80%), respectively. Both the **PG2T5** and the **PG3T5** were found to be conducting when doped with $NOBF_4$ and I_2 respectively. In this case, the ratio of dendrimer to thiophene units is 1:6, allowing more space between dendrimers and, as a consequence, better packing is expected in the solid state. Although **PG2T5** is insoluble, chunks[15] of the material could be doped by immersing the sample into a saturated solution of $NOBF_4$ in nitromethane. Four-point probe measurements obtained by placing the probes into the material indicated a resistance as low as 0.10 Ohm/square. Since **PG3T5** is soluble, thin films were drop-cast from a concentrated xylene solution and conductivities in the range of 50−100 S/cm were observed with some measurements as high as 200 S/cm.[16]

The solution UV−vis spectrum of **PG2T** in chloroform shows a single absorbance at 460 nm. It is interesting to note that although **PG2T** and poly(3-hexylthiophene) (P3HT) have a similar effective conjugation in solution (i.e., $\lambda_{max}(CHCl_3) = 456$ nm)[6a] only P3HT is conducting, thus confirming the importance of molecular order in the solid state in addition to conjugation. The solution UV−vis absorbance spectrum of **PG3T5** in THF at room temperature, shows absorbance bands at 540 and 578 nm (Figure 1). Similarly, absorbances at 530 and 578 nm are observed at room temperature in dichlorobenzene (DCB) where as the solid-state spectrum of **PG3T5** has absorbance maxima at 548 and 586 nm. Upon being heated to 150 °C, the **PG3T5** DCB solution becomes orange and the absorbance spectrum loses its vibrational structure, thus resulting in a single absorbance centered at 494 nm (Figure 1). Upon standing at room temperature, the solution quickly regains its purple/red color as well as the vibrational structure previously observed in the room-temperature UV−vis absorbance spectrum.

Size exclusion chromatography (SEC) of **PG2T** in THF (45 °C) provides a monomodal distribution with a number-average molecular weight (M_n) of 16K and a polydispersity index (PDI) of 2.3. In contrast, the size exclusion chromatogram of **PG3T5** in THF (45 °C) reveals a multimodal distribution having a broad range of molecular weights (Figure 2). By monitoring the UV−vis spectrum of the different molecular weight fractions obtained during the SEC run, it is possible to correlate the molecular weight data to the spectral data discussed previously (Figure 2). For example the λ_{max} values observed for **PG3T5** in solution at room temperature (i.e., 540 and 578 nm) are found in the high molecular weight fraction with retention times (rt) of 16 to 24 min

Scheme 2. Polymerization of the Oligothiophene Macromonomers



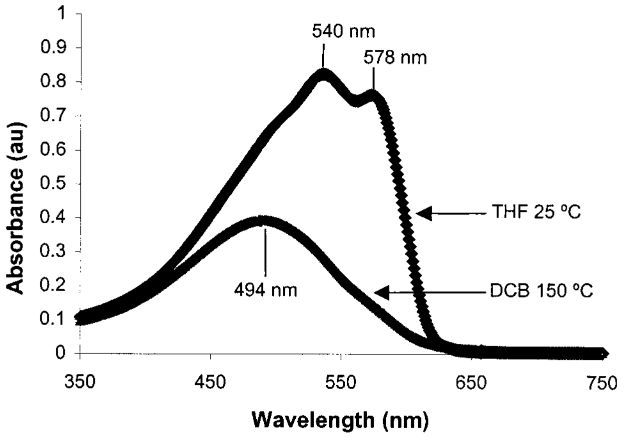


Figure 1. Solution UV–vis spectrum of **PG3T5** in THF at 25 °C and DCB at 150 °C.

while the lower molecular weight fraction with retention time = 24 to 30 min show no vibrational structure in their UV–vis spectra (i.e., single absorbance with λ_{max} ranging from 450 to 480 nm). Interestingly, isolated fractions collected by preparative SEC had a purple/red color in THF for the 16–24 min range where as the 24–30 min fractions were orange colored.

MALDI–TOF[17] analysis of isolated fractions (rt = 16–24 min) obtained by preparative SEC supports the existence of high molecular weight polymer rather than the presence of aggregates (Figure 3).[18] Molecular weights in the range of 11K, 19K, 39K and 84K were measured by MALDI–TOF spectrometry for fractions enriched with material having rt = 16–24 min. These molecular weights correspond to ca. 36, 60, 126, and 270 thiophene units respectively assuming the macromonomer repeat unit is made up of one dendron and six thiophene units (fw 1834 amu). The doubling of the molecular weight observed by MALDI–TOF is not surprising, and consistent with the condensation mechanism that is operative under the Stille reaction coupling conditions.[13a] The relatively lower molecular weight fractions, having retention times ranging from 24 to 30 min, have absorbance maxima in the 450–480 nm range, which is indicative of oligomerization of the pentathiophene macromonomer. MALDI–TOF spectra and size exclusion chromatograms of enriched fractions obtained by preparative SEC correlate well and indicate the presence of "dimer" with 11 thiophene units through to the "pentamer" with 29 thiophene units.

It is interesting to note that the vibrational structure observed in the room-temperature solution UV–vis spectrum of **PG3T5** is typically associated with aggregation,[18] yet this notion is not supported by our MALDI–TOF results. Alternatively, it is not inconceivable that polymer chains having such high molecular weights could have intramolecular "stacking" interactions that would exhibit spectroscopic features similar to those found for conventional intermolecularly aggregated species.[18d] It is fully expected that, under the conditions used for MALDI–TOF spectrometry, aggregates would break apart into their constituent components rather than fly as a single entity. This strongly supports our view that the material that elutes in the 16–24 min range is, at least in large part, a high molecular weight polymer. Although light scattering studies could shed more light on the issue of aggregation, the absorptive/emissive characteristics of the poly-

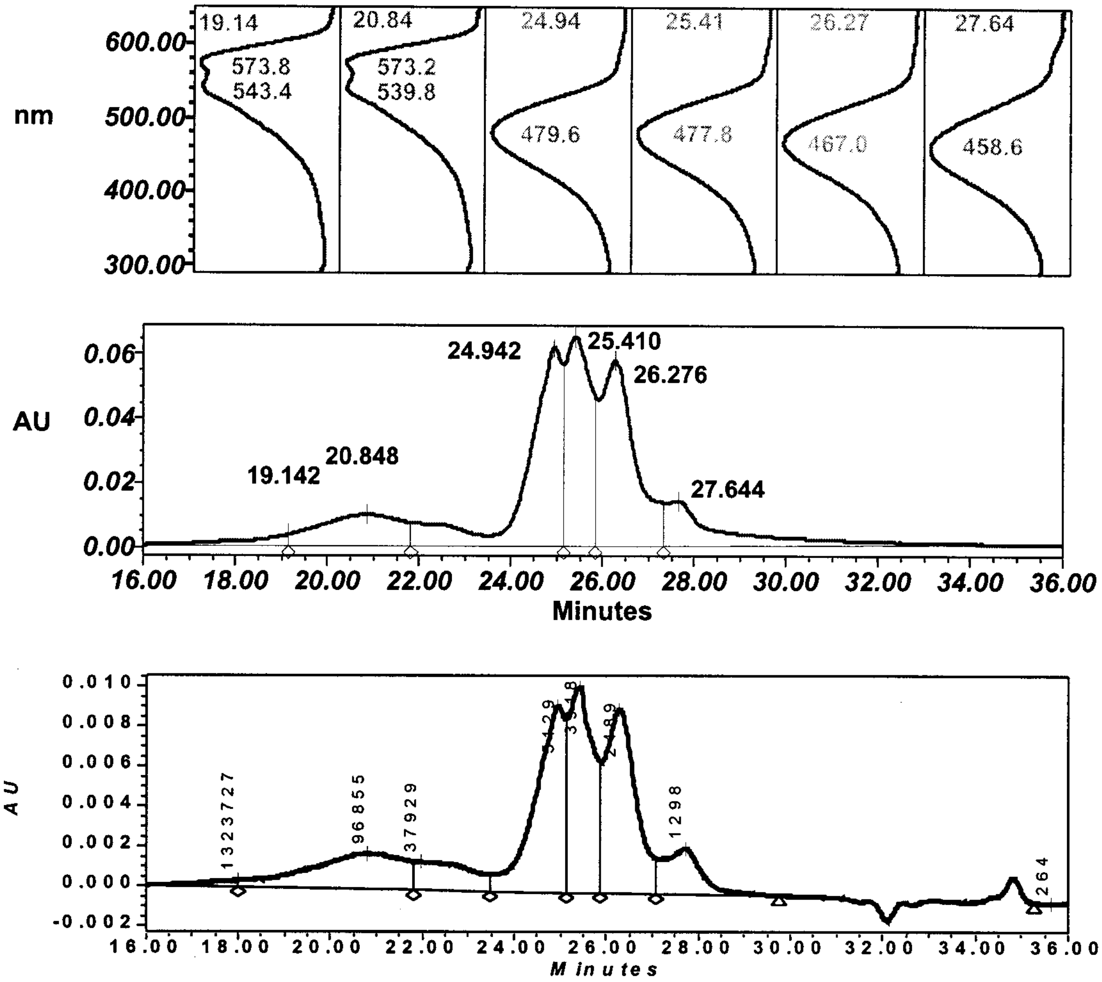


Figure 2. SEC chromatogram of **PG3T5** in THF with UV–vis spectra at varying retention times.

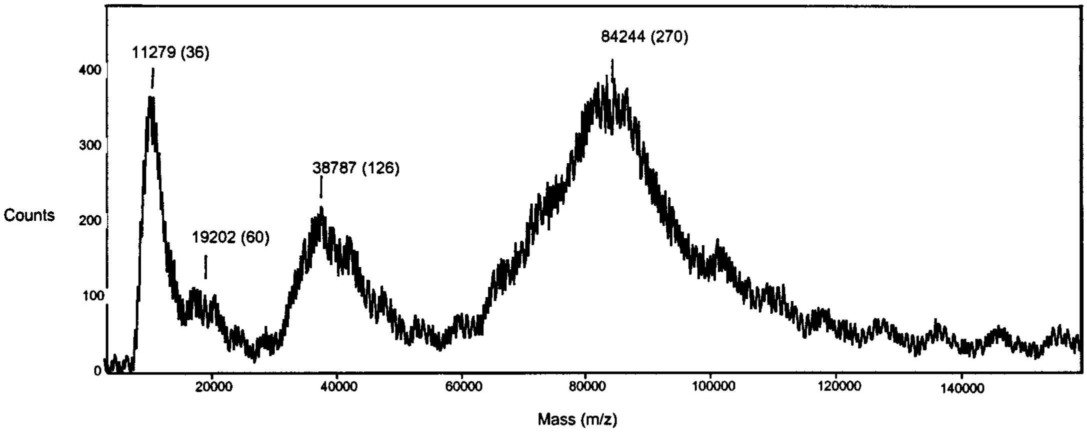


Figure 3. MALDI–TOF of 16–24 min fraction isolated by preparative SEC of **PG3T5**. In parentheses are the approximate number of thiophene units.

thiophene backbone over a broad range of the UV–vis spectrum render such experiments less than reliable.[19]

Conclusion

In summary, we have presented the successful synthesis of polythiophenes derived from oligothiophenes tethered to the focal point of G2 and G3 aliphatic ether dendrimers using a Stille coupling approach. The pentathiophene macromonomer synthesis was facilitated by the enhanced solubility and the chemical inertness provided by the aliphatic dendrimer framework and allowed the preparation of the first conducting polymer functionalized exclusively with dendritic side chains. Both the dendrimer to thiophene unit ratio and dendrimer size are essential variables that must be optimized in order to obtain a solution processable conducting polymer. An investigation of the morphology of these dendritic systems might establish whether a link exists between conductivity and the supramolecular ordering of these dendrimer–polythiophene hybrid polymers. Polythiophene-dendrimer hybrids could be potentially useful as biosensors in which the high local concentration of interacting moieties at the dendrimer surface is exploited for assays in which the detection mechanism relies on multivalent interactions (e.g., cluster effect in protein−carbohydrate interactions).[20]

Experimental Section

Materials. All reagents were purchased from Aldrich and used without further purification unless otherwise noted. P3HT was purified by Soxhlet extraction in hexanes, followed by chloroform and the chloroform fraction was isolated. 2,5-dibromo-3-thiopheneacetic acid was prepared as described previously.[10] Aliphatic ether dendrimers were prepared according to a literature procedure.[11a] NBS was recrystallized from a 1:1 acetic acid/water mixture. 2,5-Bis(trimethylstannyl)-thiophene was prepared according to a literature procedure and the product was purified by recrystallization from pentane.[12b] 5-(Trimethylstannyl)-2,2′-bithiophene was prepared according to a procedure described by Groenendaal et al.[12a] THF was distilled over sodium/benzophenone. Dichloromethane was distilled over CaH_2. *N*,*N*-Dimethylformamide (Fisher) was used as received. *n*-Butyllithium in hexanes (1.6 M) was used. All reactions were performed under argon.

Characterization. Thin-layer chromatography was performed on Merck Kieselgel 60 F_{254}. Silica used for flash chromatography was Merck Kieselgel 60 (230−400 mesh). Glass transition temperatures (T_g) were measured on a Seiko II (DSC 6200) differential scanning calorimeter (−50 to +300 °C) and taken upon the second heating (20 °C/min). Decompostion temperatures (T_{dec}) were measured on a Seiko II (SSC 5200) (25−400 °C). Infrared spectra were collected on a Mattson Genesis II FT-IR using potassium bromide with a diffuse reflectance accessory (Pike). UV−vis spectra were taken on a Hewlett-Packard HP 8453 spectrophotometer. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker DRX-500 instrument. FAB MS (low resolution) was done on a Micromass 70-SE double focusing mass spectrometer (EB geometry) with a nitro benzyl alcohol matrix (NBA). FAB MS (high resolution) was done on a Micromass ZAB2-EZ double focusing mass spectrometer (BE geometry). MALDI−TOF data were collected on a PE Perseptive Biosystems Voyager-DE instrument in positive ion mode (Foster City, CA). The instrument was calibrated using Bovine Insulin and the matrix system was dithranol.[17] Size exclusion chromatography was carried out on a Waters GPC 150-CV plus system (Milford, MA) with an attached M486 tunable absorbance detector ($\lambda = 254$ nm). Polystyrene standards (18) were used for calibration and the mobile phase was tetrahydrofuran (1 mL/min, 45 °C). A bank of four PL Gel columns (5 μm) from Polymer Laboratories (Amherst, MA) was used: 100 Å, 100 Å, 500 Å, and a Mixed C. The SEC/UV−vis experiments were performed using a system consisting of a M510 Waters solvent delivery system, M717 Waters autosampler, and a M996 Waters photodiode array detector ($\lambda =$ 215−650 nm). A bank of four PL Gel columns (5 μm) from Polymer Laboratories was used: 100 Å, 100 Å, 10^3 Å, and 10^5 Å. Eighteen polystyrene standards were used for calibration, and the mobile phase was tetrahydrofuran (1 mL/minute, 45 °C). Preparative SEC was done on a semipreparative GPC system consisting of a M510 Waters solvent delivery system and a U6K Waters manual injector (flow rate of 3.6 mL/min, 25 °C). The column used was an SDV linear column (10 μm, 20 × 600 mm) from Polymer Standard Service GmbH (Mainz, Germany). Elemental analyses were performed at M−H−W Laboratories, P.O. Box 15149, Phoenix, AZ 85060. Film thickness (3−5 μm) was measured on a Tenkor α step. Conductivity measurements were performed on a Signatone four-point probe, model S-301.

Sample Preparation for Conductivity Measurements. Thin films were cast onto quartz wafers from xylenes solutions. The solvent was allowed to evaporate in air for 2 h. The wafers were then placed under high vacuum overnight. Doping with iodine vapor was done by placing the quartz wafers in a sealed jar containing iodine crystals for 5 h. Doping with $NOBF_4$ was done by immersing the insoluble sample into a saturated solution of $NOBF_4$ in nitromethane for 3 h, followed by rinsing with nitromethane and pumping down under high vacuum for 1 h.

[G-3]-2,5-Dibromothiophene-3-acetate (1). To an oven-dried flask was added 0.0940 g (0.313 mmol) of 2,5-dibromothiophene-3-carboxylic acid, 0.4072 g (0.313 mmol) of [G-3]-OH and 0.020 g (0.007 mmol) of DPTS. The mixture was dissolved in 1 mL of CH_2Cl_2 and placed under argon before adding 0.0475 g (0.313 mmol) of DCC and allowing the solution to stir at room temperature for 3 h. The reaction mixture was filtered through Celite and the solvent was removed. The crude product was purified on silica using a step gradient of ethyl acetate/hexanes (1:4 to 2:3) as the eluant. The solvent was evaporated and the colorless oil was dried in vacuo overnight (0.371 g, 0.234 mmol, 75%). IR (KBr): 3086, 3062, 3031, 2870, 1737, 1496, 1452, 1365, 1112, 908, 738, 699, 608, 475 cm^{-1}. UV−vis ($CHCl_3$): $\lambda_{max} = 244$ nm. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45−7.20 (m, 40H), 6.87 (s, 1H) 4.49 (s, 16H), 4.12 (d, $J =$ 6 Hz, 2H), 3.65−3.20 (bm, 38H), 2.14 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.2, 138.3, 134.5, 131.4, 128.2, 128.0, 127.43, 127.38, 110.8, 110.5, 78.3, 73.2, 69.9, 69.4, 68.9, 68.5, 63.5, 40.8, 39.1, 34.8. HRMS (FAB): calcd for $C_{86}H_{100}O_{16}SBr_2$ (MH^+), 1579.5177; found, 1579.5117. MS (SEC): $M_n = 1200$; PDI = 1.00. Anal. Calcd for $C_{86}H_{100}O_{16}SBr_2$: C, 65.31; H, 6.37. Found C, 65.18; H, 6.23.

[G-3] 2,2′:5′,2″:5″,2‴:5‴,2⁗-Quinquethiophene-3″-acetate (2). A 0.300 g (0.189 mmol) sample of **1** and 0.152 g (0.462 mmol) of 5-(trimethylstannyl)-2,2′-bithiophene were charged into a round-bottom flask with 2 mL of DMF. The solution was deareated under vacuum and backfilled with argon five times prior to the addition of $Pd(PPh_3)_2Cl_2$ catalyst (2−5 mol %). The resulting solution was heated to 90 °C and stirred overnight. DMF was removed by distillation under reduced pressure. The resulting oil was first filtered through silica in CH_2Cl_2, and subsequently washed through in ethyl acetate prior to chromatography on silica using a step gradient going from (1:4) ethyl acetate/hexanes to (2:3) ethyl acetate/hexane. The solvent was evaporated and the red oil was dried overnight in vacuo (0.273 g, 0.156 mmol, 82%). IR (KBr): 3086, 3062, 3030, 1735, 1496, 1453, 1366, 1268, 1096, 792, 737, 698, 609, 468 cm^{-1}. UV−vis ($CHCl_3$): $\lambda_{max} = 400$ nm. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30−7.11 (m, 40H), 7.10−7.08 (2 × d, 2H), 7.06 (dd, $J =$ 1 and 3.6 Hz, 1H), 7.05 (dd, $J =$ 1 and 3.6 Hz, 1H), 702−6.98 (m, 3H), 6.94 (2 × d, 2H) 7.05 (2 × d, 2H) 4.38 (s, 16H), 4.08 (d, $J =$ 5.8 Hz, 2H), 3.62 (s, 2H), 3.60−3.13 (m, 36) 2.10−1.98 (2 × m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 138.4, 137.9, 136.9, 136.7, 136.6, 135.4, 135.3, 133.5, 131.8, 131.0, 128.2, 127.9, 127.9, 127.5, 127.4, 127.3, 126.8, 124.7, 124.6, 124.5, 124.4, 124.3, 123.9, 123.8, 78.3, 73.2, 69.9, 69.4, 69.0, 68.5, 63.5, 40.8, 39.2, 34.9. HRMS (FAB): calcd for $C_{102}H_{110}O_{16}S_5$, 1750.6397; found, 1750.6346. MS (SEC): $M_n =$ 1300; PDI = 1.00. Anal. Calcd for $C_{102}H_{110}O_{16}S_5$: C, 69.92; H, 6.33. Found C, 70.06; H, 6.13.

[G-3]-Dibromo-5,5⁗-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene-3″-acetate (3). A 0.7118 g (0.402 mmol) sample of **2** was dissolved in 2.0 mL of DMF and 0.143 g (0.805 mmol) of NBS was subsequently added. After allowing the solution to stir at room temperature, overnight, under argon, the reaction mixture was diluted in diethyl ether and extracted three times with water to remove the DMF. The ether layer was dried over $MgSO_4$, filtered and evaporated. The crude product was dissolved in CH_2Cl_2 and chromatographed on silica using a step gradient of ethyl acetate/hexanes as the eluant (1:4 to 1:1). The solvent was evaporated and the product was dried in vacuo overnight to yield a red oil (0.736 g, 0.382 mmol, 95%). IR (KBr): 3086, 3061, 3029, 2860, 1737, 1495, 1452, 1366, 1251, 1205, 1099, 836, 798, 737, 698, 609, 465 cm^{-1}. UV−vis ($CHCl_3$): $\lambda_{max} = 400$ nm. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30−7.10 (m, 40H), 7.02−7.00 (2 × d, 2H), 6.96−6.94 (2 × d, 2H) 6.89−6.85 (3 × d, 3H), 6.81−6.79 (2 × d, 2H), 4.41 (s, 16H), 4.15 (d, $J =$ 5.5 Hz, 2H), 3.63 (s, 2H) 3.58−3.18 (bm, 36H), 2.15−2.00 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.2, 138.4, 138.2, 136.8, 135.7, 135.5, 135.4, 133.9, 131.7, 131.3, 130.8, 130.7, 128.3, 128.1, 127.5, 127.43, 127.36, 127.0, 124.6,3, 124.61, 124.0, 123.9, 111.3, 111.2, 78.3, 73.2, 70.0, 69.5, 69.0, 68.5, 63.6, 40.8, 39.2, 34.9. MS (SEC): $M_n = 1300$; PDI = 1.00. Anal. Calcd for $C_{102}H_{108}O_{16}S_5Br_2$: C, 64.14; H, 5.70. Found C, 64.24; H, 5.46.

PG2T. A round-bottom flask was charged with 0.5469 g (0.608 mmol) of G2 monothiophene dibromide,[10] 0.2493 g (0.608 mmol) of 2,5-bis(trimethylstannyl)thiophene, and 3 mL of DMF. The solution was deareated under vacuum and backfilled with argon five times prior to the addition of Pd-$(PPh_3)_2Cl_2$ catalyst (5−10 mol %). The resulting solution was heated to 90 °C and stirred for 24 h. The reaction mixture was precipitated directly into methanol and filtered. The red solid was Soxhlet extracted with MeOH for 1 day followed by chloroform. The chloroform fraction was evaporated and the polymer was dried overnight in vacuo. The product was isolated as a lustrous greenish-red material (0.4233 g, 0.517 mmol, 85%). T_g (DSC): −13.1 °C. T_{dec} (TGA): 350 °C. IR (KBr): 3087, 3060, 3029, 2864, 1735, 1496, 1453, 1365, 1270, 1096, 1027, 910, 800, 738, 698, 610, 464 cm^{-1}. UV−vis ($CHCl_3$) $\lambda_{max} = 460$ nm. ^1H NMR (500 MHz, $CDCl_3$): δ 7.40−7.16 (m, 23H), 4.60 (s, 8H), 4.15 (m, 2H), 3.65−3.20 (bm, 16H), 2.17 (m, 1H). MS (SEC): $M_n = 16\,300$; PDI = 2.30.

PG2T5. A round-bottom flask was charged with 0.5123 g (0.418 mmol) G2 pentathiophene dibromide,[10] 0.1713 g (0.418 mmol) of 2,5-bis(trimethylstannyl)thiophene, and 2.1 mL of DMF. The solution was deareated under vacuum and backfilled with argon five times prior to the addition of $Pd(PPh_3)_2$-Cl_2 catalyst (5−10 mol %). The resulting solution was heated to 90 °C and stirred for 24 h. The red gelatinlike material obtained and was Soxhlet extracted with CH_2Cl_2 for 2 days and dried under vacuum for 2 days. The insoluble product was isolated as a malleable, lustrous, greenish-red material with a metallic appearance (0.4521 g, 0.395 mmol, 94%). T_g (DSC): −9.1 °C. T_{dec} (TGA): 356 °C. Four-point probe bulk resistance 0.10 Ω/sq (doped with $NOBF_4$).

PG3T. A round-bottom flask was charged with 0.5284 g (0.331 mmol) **1**, 0.1355 g (0.331 mmol) of 2,5-bis(trimethylstannyl)thiophene, and 3.0 mL of DMF. The solution was deareated under vacuum and backfilled with argon five times prior to the addition of $Pd(PPh_3)_2Cl_2$ catalyst (5−10 mol %). The resulting solution was heated to 90 °C and stirred for 24 h. The viscous reaction mixture was poured directly into methanol and the solvent was decanted off (product oiled out). The red oil was taken up in dichloromethane, the solvent was evaporated and the polymer was dried overnight in vacuo. The product was isolated as a red oil (0.402 g, 0.265 mmol, 80%). T_g (DSC): −16.1 °C. T_{dec} (TGA): 361 °C. IR (KBr): 3086, 3061, 3029, 2864, 1736, 1496, 1453, 1366, 1260, 1094, 1027, 910, 838, 796, 738, 698, 610, 465 cm^{-1}. UV−vis ($CHCl_3$): $\lambda_{max} = 450$ nm. ^1H NMR (500 MHz, $CDCl_3$): δ 7.40−7.05 (m, 43H), 4.45 (m, 19H), 4.15 (m, 2H), 3.80−3.15 (bm, 35H), 2.17 (m, 3H). MS (SEC): $M_n = 9500$; PDI = 2.00.

PG3T5. A round-bottom flask was charged with 0.2889 g (0.150 mmol) of **3**, 0.0614 g (0.150 mmol) of 2,5-bis(trimethylstannyl)thiophene, and 2.0 mL of DMF. The solution was deareated under vacuum and backfilled with argon five times prior to the addition of $Pd(PPh_3)_2Cl_2$ catalyst (5−10 mol %). The resulting solution was heated to 90 °C and stirred for 24 h. The viscous reaction mixture was precipitated directly into methanol and filtered. The red solid was Soxhlet extracted with MeOH for 1 day followed by chloroform. The chloroform fraction was evaporated and the polymer was dried overnight in vacuo. The product was isolated as a lustrous greenish-red solid (0.223 g, 0.121 mmol, 80%). T_g (DSC): −17.0 °C. T_{dec} (TGA): 368 °C. IR (KBr): 3086, 3063, 3029, 2863, 1735, 1491, 1453, 1364, 1267, 1099, 1027, 834, 793, 738, 698, 609, 463 cm^{-1}. UV−vis (THF): 540 and 578 nm. ^1H NMR (500 MHz, $CDCl_3$ at 50 °C): δ 7.55−7.00 (bm, 51H), 4.60−4.30, (bs, 16H) 4.28−4.20 (bs, 2H), 3.80−3.20 (m, 38H), 2.20−2.05 (m, 3H). MS (SEC): $M_n = 3800$; PDI = 13.

Acknowledgment. We thank Dr. Mani Jayaraman and Dr. René Janssen (Technical University of Eindhoven) for valuable discussions, Roger Su (UC Berkeley) for assistance with the conductivity measurements, and Dr. Nikolai Vladimirov (UC Berkeley) for the preparative SEC experiments. Financial support by the Director, Office of Energy Research, Office of Science, Division of Materials Sciences, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, and the Air Force Office of Scientific Research (MURI program) is gratefully acknowledged.

References and Notes

(1) (a) Chiang, C. K.; Fincher, C. R.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Lewis, E. J.; Gau, S. C.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1977**, *39*, 1098. (b) *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds; Marcel Dekker: New York, 1998. (c) Feast, W. J.; Tsibouklis, J.; Pouwer, K. L.; Groenendaal, L.; Meijer, E. W. *Polymer* **1996**, *37*, 5017.

(2) (a) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539. (b) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 402.

(3) (a) [general topics] Scott, J. C. *Science* **1997**, *278*, 2071. (b) [sensor] Swager, T. M. *Acc. Chem. Res.* **1998**, *31*, 201. (c) [photodiode] Roman, L. S.; Andersson, M. R.; Yohannes, T.; Inganäs, O. *Adv. Mater.* **1997**, *9*, 1164. (d) [photolithography of a conducting polymer] Yu, J.; Abley, M.; Yang, C.; Holdcroft, S. *Chem. Commun.* **1998**, 1503. (e) [biosensor] Hiller, M.; Kranz, C.; Huber, J.; Bäuerle, P.; Schuhmann, W. *Adv. Mater.* **1996**, *8*, 219. (f) [field effect transitor] Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *280*, 1741. (g) [field effect transistor] Bao, Z.; Lovinger, A. J. *Chem. Mater.* **1999**, *11*, 2607. (f) [organic smart pixel] Dodabalapur, A.; Bao, Z.; Makhija, A.; Laquindanum, J. G.; Raju, V. R.; Feng, Y.; Katz, H. E.; Rogers, J. *Appl. Phys. Lett.* **1998**, *73*, 142.

(4) (a) Jen, K.-Y.; Miller, G. G.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1346. (b) Elsenbaumer, R. L.; Jen, K.-Y.; Oboodi, R. *Synth. Met.* **1986**, *15*, 169. (c) Yamamoto, T.; Morita, A.; Miyazaki, Y.; Maruyama, T.; Wakayama, H.; Zhou, Z.; Nakamura, Y.; Kanbara, T. *Macromolecules* **1992**, *25*, 1214. (d) Gill, R. E.; Malliaras, G. G.; Wildeman, J.; Hadziioannou, G. *Adv. Mater.* **1994**, *6*, 132. (e) Souto Maior, R. M.; Hinkelmann, K.; Eckert, H.; Wudl, F. *Macromolecules* **1990**, *23*, 1268. (f) Barbarella, G.; Bongini, A.; Zambianchi, M. *Macromolecules* **1994**, *27*, 3039.

(5) (a) Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D. *Adv. Mater.* **1999**, *11*, 250. (b) McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93. (c) Lowe, R. D.; McCullough, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, 70.

(6) (a) Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233. (b) Chen, T.-A.; O'brien. R. A.; Rieke, R. D. *Macromolecules* **1993**, *26*, 3462. (c) Chen, T.-A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087.

(7) (a) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules: Concepts, Synthesis, Perspectives*; VCH: Weinheim, Germany, and New York, 1996. (b) Emrick, T.; Fréchet, J. M. J. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 15. (c) Fisher, M.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 884. (d) Frey, H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2193. (e) Matthews, O. A.; Shipway, A. N.; Stoddart, J. F. *Prog. Polym. Sci.* **1998**, *23*, 1. (f) Schlüter, A.-D. *Top. Curr. Chem.* **1998**, *197*, 165.

(8) For other examples on the use of dendrimers as side chains with conjugated polymers see: (a) [antenna effect and site isolation with poly(phenylene ethynylene)] Sato, T.; Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **1999**, *121*, 10658. (b) [liquid crystallinity and site isolation with poly(*p*-phenylene vinylene)] Bao, Z.; Amundson, K. R.; Lovinger, A. J. *Macromolecules* **1998**, *31*, 8647. (c) [site isolation with oligotriacetylenes] Schenning, A. P. H. J.; Martin, R. E.; Ito, M.; Diederich, F.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M. *Chem. Commun.* **1998**, 1013. (d) [shape-persistent polymers with poly(*p*-phenylene)] Stocker, W.; Karakaya, B.; Schürmann, B. L.; Rabe, J. P.; Schlüter A. D. *J. Am. Chem. Soc.* **1998**, *120*, 7691.

(9) Malenfant, P. R. L.; Groenendaal, L.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1998**, *120*, 10990.

(10) Malenfant, P. R. L.; Jayaraman, M.; Fréchet, J. M. J. *Chem. Mater.* **1999**, *11*, 3420.

(11) (a) Jayaraman, M.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1998**, *120*, 12996. (b) Grayson, S. M.; Jayaraman, M.; Fréchet, J. M. J. *Chem. Commun.* **1999**, 1329.

(12) (a) Groenendaal, L.; Bruining, M. J.; Hendrickx, E. H. J.; Persoons, A.; Vekemans, J. A. J. M.; Havinga, E. E.; Meijer, E. W. *Chem. Mater.* **1998**, *10*, 226. (b) Seitz, D. E.; Lee, S.-H.; Hanson, R. N.; Bottaro, J. C. *Synth. Commun.* **1983**, *13*, 121.

(13) (a) Bao, Z.; Chan, W. K.; Yu, L. *J. Am. Chem. Soc.* **1995**, *117*, 12426. (b) Bjørnholm. T.; Greve, D. R.; Reitzel, N.; Hassenkam, T.; Kjaer, K.; Howes, P. B.; Larsen, N. B.; Bøgelund, J.; Jayaraman, M.; Ewbank, P. C.; McCullough, R. D. *J. Am. Chem. Soc.* **1998**, *120*, 7643.

(14) Based on the generally accepted mechanism for Stille coupling reactions, we anticipate that at least 5−10% homocoupling of the thienyl-stannane derivative will occur during the polymerization. The occurrence of thienyl-stannane homocoupling will result in the insertion of one extra thiophene ring between the dendritic substituents. In light of the relatively low extent of homocoupling and the minimal degree of substitution along the polythiophene backbone, we do not expect this to significantly affect the overall polymer structure, especially for polymers derived from the pentathiophene macromonomers. For a more detailed discussion on the effects of homocoupling, see ref 13a.

(15) It is interesting to note that **PG2T5** does not precipitate out of solution during the polymerization, but rather gels and takes the shape of the flask during the reaction, thus forming a malleable, continuous material having a lustrous greenish-red metallic appearance. We do not believe that this is due to cross-linking but rather due to the unique properties imparted by the aliphatic ether dendrimers.

(16) As a comparison, a commercial sample of poly(3-hexylthiophene) was examined in parallel and an average conductivity of 5 S/cm was obtained. Prior to use, poly(3-hexylthiophene) was purified by Soxhlet extraction in hexanes followed by chloroform and the chloroform fraction was used for the conductivity measurement. Literature values for poly(3-alkylthiophene) are in the range of 10^2-10^3 S/cm (see ref 5b).

(17) For a detailed molecular weight analysis of poly(3-alkylthiophenes) by MALDI−TOF see: Liu, J.; Loewe, R. S.; McCullough, R. D. *Macromolecules* **1999**, *32*, 5777.

(18) (a) Langeveld-Voss, B. M. W.; Waterval, R. J. M.; Janssen, R. A. J.; Meijer, E. W. *Macromolecules* **1999**, *32*, 227. (b) Langeveld-Voss, B. M. W.; Christiaans, M. P. T.; Janssen, R. A. J.; Meijer, E. W. *Macromolecules* **1998**, *31*, 6702. (c) Yue, S.; Berry, G. C.; McCullough, R. D. *Macromolecules* **1996**, *29*, 933. (d) Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1071.

(19) Wyatt, P. J. *Anal. Chim. Acta* **1993**, *272*, 1.

(20) (a) Dimick, S. M.; Powell, S. C.; McMahon, S. A.; Moothoo, D. N.; Naismith, J. H.; Toone, E. J. *J. Am. Chem. Soc.* **1999**, *121*, 10286 and references therein. (b) Roy, R. *Top. Curr. Chem.* **1997**, *187*, 241.

MA000003W