Macromolecules **2000,** *33,* 5300−5302

Notes

Synthesis of a Terminally Functionalized Bromothiophene Polyphenylene Dendrimer by a Divergent Method

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Received February 14, 2000
Revised Manuscript Received May 3, 2000

Introduction

The chemistry of well-defined highly branched dendrimers has developed rapidly since the pioneering work by Vogtle,[1] Tomalia,[2] and Newkome.[3] There are two general approaches to synthesize dendrimers. One is the divergent synthesis which involves developing the dendrimer structure from a core outward. The other is the convergent synthesis which begins from the outer surface and builds up the dendrimer, with the final step involving coupling of preformed dendrions with a central molecular core.[4] Using this convergent approach, polyphenylene dendrimers with up to 46 benzene rings have been synthesized.[5] Other conjugated dendrimers such as poly(phenylacetylene)s[6] and poly(phenylenevinylene)s[7] have been also synthesized by the convergent method. Perfluorinated polyphenylene dendrimers have been synthesized recently.[8]

Another type of branched polymer having linear polymer arms attached to a common core is a star polymer.[9] We have synthesized star poly(3-hexylthiophene) using hyperbranched polyphenylene as a core.[10] This hyperbranched polyphenylene core was synthesized by a one-step reaction from an AB_2 type monomer.[11] The star polymer inherits the relatively broad molecular weight distribution of the core from which it is derived. For the purpose of investigating the properties of the star polymer, it is desirable that it have a more controlled structure. Therefore, a polyphenylene dendrimer core with a precise structure is desired. Here we report the synthesis of a polyphenylene dendrimer that is terminally functionalized with bromothiophene. The dendrimer was synthesized by a stepwise divergent approach using the palladium-catalyzed coupling reaction of aryl−zinc chloride and aryl bromide. This alternative approach is useful for synthesizing polyphenylene dendrimers having sensitive surface terminal functional groups. This facile synthesis can be expanded to higher generations of polyphenylene dendrimers.

Results and Discussion

The goal of this work is to synthesize a polyphenylene dendrimer with 12 bromothiophene terminal groups. In earlier work, the synthesis of polyphenylene dendrimers was conducted by following a convergent approach developed by Miller et al.[5] The terminal building block compound, 3,5-bis(thienyl)-1-trimethylsilylbezene, was synthesized. However, when we tried to convert the trimethylsilyl group to a boronic acid group by the BBr_3/KOH treatment, we found that the thiophene ring was not stable under the conditions used. Therefore, due to the sensitivity of the thiophene group, this convergent approach was not feasible for our purpose.

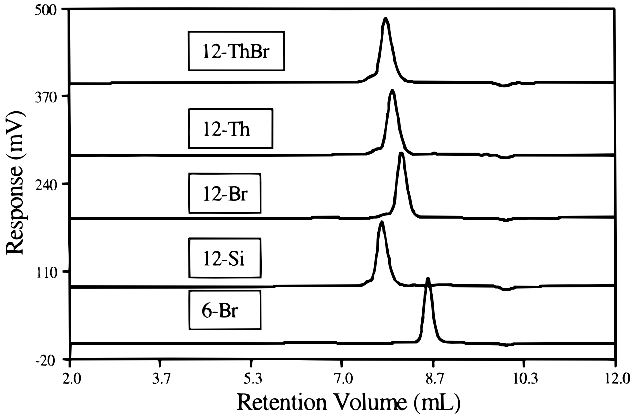
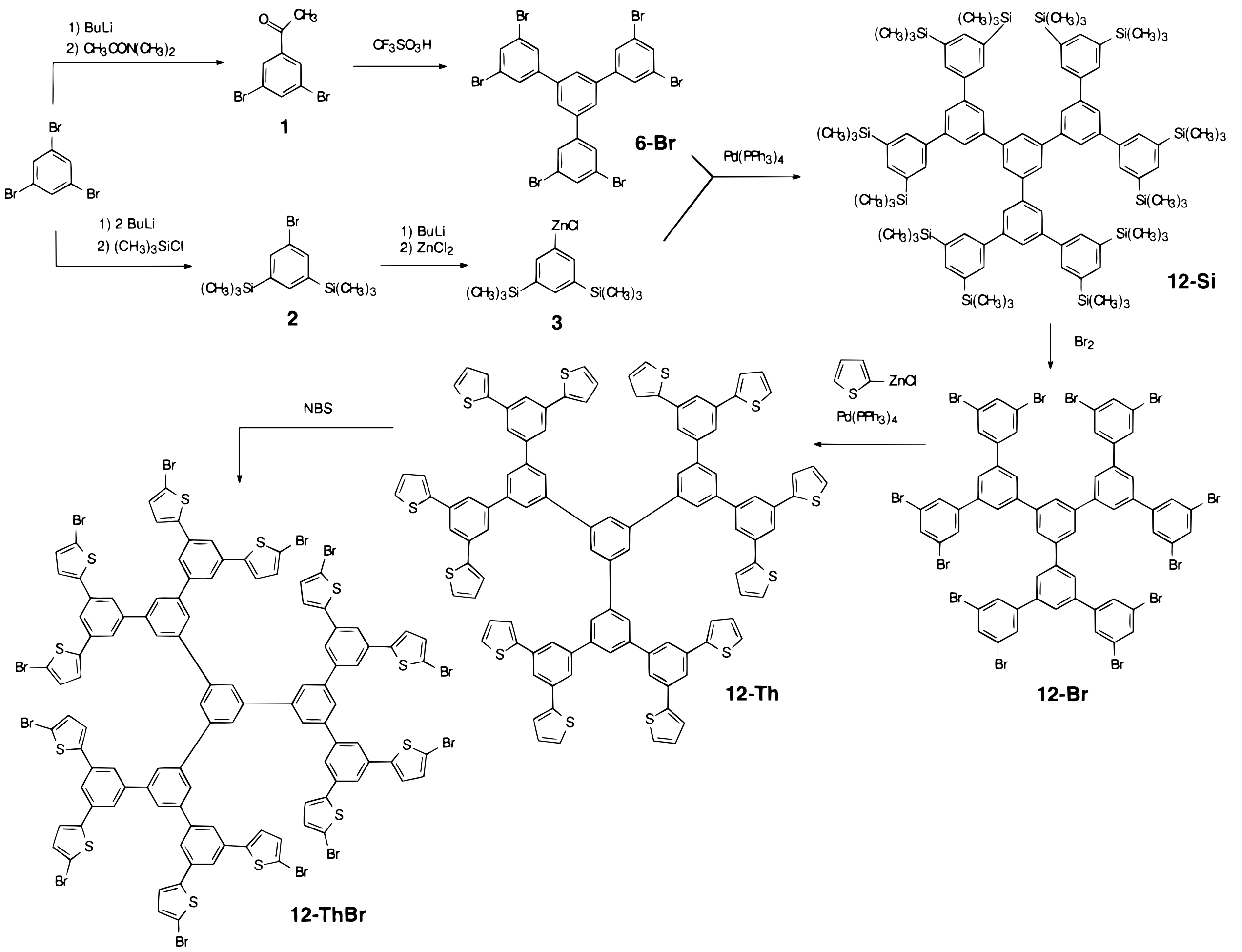


Figure 1. SEC chromatograms of dendrimers: **6-Br**, **12-Si**, **12-Br**, **12-Th**, and **12-ThBr**.

The synthesis of the target dendrimer was carried out as outlined in Scheme 1. 1,3,5-Tribromobenzene was monolithiated by butyllithium, followed by reaction with *N*,*N*-dimethylacetamide which yielded 3,5-dibromoacetophenone (**1**). In the early stage of the work, **6-Br** was synthesized by condensation of **1** with $K_2S_2O_7/H_2SO_4$ at 180 °C.[5] The reaction yield was very low (15%), and the workup procedure was very tedious. This step was optimized by a different procedure with trifluoromethanesulfonic acid as the catalyst for condensation.[12] An improvement in the reaction yield of **6-Br** (48%) was achieved, and the workup process was also simplified. 1,3,5-Tribromobenzene was reacted with 2 equiv of butyllithium followed by quenching with trimethylsilyl chloride to form 3,5-bis(trimethylsilyl)bromobenzene (**2**). **2** was isolated by vacuum distillation. However, it still contained about 13% tris(trimethylsilyl)benzene as a byproduct. Recrystallization did not improve the purity. Since this tris(trimethylsilyl)benzene does not interfere with next reaction step, no further purification was attempted. The distilled product was used for the reaction in the next step. The bromo group on **2** was converted to zinc chloride, **3**, by treatment with butyllithium followed by zinc chloride. **3** was coupled with **6-Br** under the catalysis of $Pd(PPh_3)_4$ in THF. The reaction progress was monitored by SEC, and the results indicated that the reaction was completed in 18 h. Since the reaction involved multiple coupling reactions between one molecule of **6-Br** and six molecules of **3**, it was expected the reaction would proceed slowly. However, the relatively fast reaction rate observed may be due to the high reactivity in the Negishi coupling reaction. **12-Si** was isolated from low molecular weight

10.1021/ma000268a CCC: $19.00 © 2000 American Chemical Society
Published on Web 06/17/2000

Scheme 1



impurities by precipitation in methanol.

The transformation of the trimethylsilyl group to bromide was accomplished by treatment with bromine at room temperature.[13] The reaction progress was monitored by carrying out a small-scale reaction in a NMR tube in deuterated solvent. It was determined that the reaction rate was very fast, and the conversion was completed in less than an hour. However, when the reaction was scaled up, it took a longer time to complete the conversion. Capping the **12-Br** with thiophene to form **12-Th** was accomplished by the Negishi coupling reaction with 2-zinc chloride thiophene under the catalysis of $Pd(PPh_3)_4$ in THF. To ensure the complete conversion, a longer reaction time (2 days) was used. A quantitative yield was obtained for this step of the reaction. **12-Th** was converted to **12-ThBr** by reaction with *N*-bromosuccinimide (NBS) in high yield. All the reactions from **6-Br** to **12-ThBr** gave high yields. The purification of dendrimers **12-Br**, **12-Th**, and **12-ThBr** required simple precipitation. No column chromatography was required. Such a facile procedure has made it possible to further scale-up the reactions.

The molecular weights of these dendrimers were determined by SEC. The chromatograms are shown in Figure 1, and the results are summarized in Table 1. As can be seen from the table, the SEC molecular weights are in good agreement with theoretical values for all the dendrimers except **12-ThBr**, which is higher. This may be due to a small fraction of high molecular weight material in the **12-ThBr** sample which gives a strong light scattering signal and therefore the higher molecular weight value. One interesting property of

Table 1. SEC Characterization and Elemental Analysis Results on Dendrimers

	formula	theor mol wt	M_n	M_w/M_n	retention vol (mL)	elemental analysis[a]				
						C %	H %	Br %	S %	Si %
6-Br	$C_{24}H_{12}Br_6$	780	720	1.18	8.57	37.02 (36.97)	1.53 (1.55)	61.05 (61.48)		
12-Si	$C_{96}H_{138}Si_{12}$	1629	1630	1.14	7.73	69.94 (70.77)	8.41 (8.54)			20.99 (20.69)
12-Br	$C_{60}H_{30}Br_{12}$	1710	1780	1.16	8.10	41.92 (42.15)	1.72 (1.77)	55.99 (56.08)		
12-Th	$C_{108}H_{66}S_{12}$	1748	1890	1.17	7.93	73.59 (74.19)	3.68 (3.80)		21.96 (22.01)	
12-ThBr	$C_{108}H_{54}Br_{12}S_{12}$	2695	3450	1.18	7.82	48.34 (48.13)	1.89 (2.02)	34.42 (35.58)	14.14 (14.27)	

[a] Calculated numbers are shown in parentheses.

these dendrimers is their molecular sizes, as indicated by the retention volume in SEC. Smaller retention volume indicates larger hydrodynamic size because the sample is eluted from the size exclusion column faster. That **6-Br** has the smallest size is obvious. The **12-Si** sample has the second smallest molecular weight but shows the smallest retention volume. Considering the bulky trimethysilyl group, this is not too surprising. When comparing trimethylsilyl to bromine and thiophene, the larger size of **12-Si** compared to **12-Br** and **12-Th** is understandable. However, the bromothiophene group is quite big and is longer than trimethylsilyl. The molecular weight of **12-ThBr** is also much higher than that of **12-Si**. Despite these facts, **12-ThBr** still passes the column slower than **12-Si**. This may due to the steric shielding effect of the bulky trimethylsilyl groups which prohibit the **12-Si** molecules from interacting efficiently with the cross-linked polystyrene gel in the size exclusion column, and so it passes the column more quickly. This phenomenon also demonstrates that the dendrimers' properties are influenced greatly by the surface functional groups.

All the structural transformations are confirmed by ^{1}H NMR. **6-Br** shows a single peak in the aromatic range due to the similarities of these protons. **12-Si** has two sets of peaks from trimethylsilyl and the phenylene. The integration ratio of these two peaks is consistent with the structure of 108 methyl protons and 30 phenylene protons. When the conversion from **12-Si** to **12-Br** was not complete, a methyl proton signal remained in the product. The pure **12-Br** product was confirmed by the complete disappearance of these methyl protons. The **12-Th** sample shows two groups of peaks in the aromatic range. The thiophene protons appear at the higher field of 7.2−7.6. The phenylene protons appear at 7.6−8.0. The two group of peaks overlap, so integration was inconclusive. However, the intensity of the thiophene proton signals is very high, indicating a full substitution reaction. The **12-ThBr** sample shows the reduced thiophene proton signal intensity in accord with the bromo substitution.

The elemental analysis results for these dendrimer samples are also included in Table 1. It can be seen from this table that the data are fully consistent with the expected structures. The conversion from **6-Br** to **12-Si** is a complete reaction demonstrated by the expected silicon level in the **12-Si** sample. The conversion from **12-Si** to **12-Br** was also demonstrated by the expected bromine level in **12-Br**. The complete conversion from **12-Br** to **12-Th** was confirmed by the expected sulfur content in the **12-Th**. The found bromine level in **12-ThBr** is slightly lower than calculated value that may due to the incomplete bromination reaction. However, the found Br % level is 97% of the calculated Br % in **12-ThBr**.

In conclusion, a polyphenylene dendrimer with terminal bromothiophene groups was successfully synthesized by a divergent approach. The reaction yields are high, and the purification procedure for products are simple. This synthetic method can be extended further to the higher generations of dendrimer synthesis. The application of this dendrimer for star polymer synthesis is under investigation and will be reported separately.

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

Supporting Information Available: Text detailing the synthesis and characterization of all polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA000268A