

Toward Dendrimers with Cylindrical Shape in Solution

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Abstract: Three approaches for the synthesis of dendrimers with poly(*p*-phenylene)-PPP derived cores are described. The respective limitations of these approaches are assessed in view of the goal of this research: to make available structurally perfect, high molecular weight polymers with a dense sequence of sterically demanding dendrons.

Introduction

Research on dendrimers first focused on synthetic issues concerning this new class of macromolecules; both academic and industrial chemists discovered divergent, convergent, and divergent/convergent growth patterns and determined their intrinsic advantages and deficiencies.¹ Now that a broad range of dendrimers is available, some even commercially, focus has shifted from merely synthetic problems to questions such as what are dendrimers good for and where are these unique compounds superior to known systems? Dendrimers were then investigated, e.g., as large compartmented hosts for drug delivery, as carriers for catalytically active sites in flow reactors, and for charge or energy transfer purposes.² Practically all dendrimers known today are believed to attain a more or less spherical structure in solution. Recently, the question arose if dendrimers can be made which do not have a spherical but rather a cylindrical shape in solution.³ Such a goal would not only be a challenge for synthetic chemistry per se because of the enormous degree of structure control required but would also contribute to the field of supramolecular chemistry in that reasonably functionalized macrocylinders may act as new constituents for “giganto” micelles, vesicles, membranes, etc.

In convergent strategy, preformed dendritic fragments (dendrons) are reacted with small, “dot-like” core molecules until complete coverage is reached.⁴ When dendrons were attached to polymeric cores instead, a macromolecule could be formed with a backbone which is wrapped about by wedges that increasingly branch as they go from the inner to the outer regions. Depending upon the backbone stiffness, the degree of coverage, the size of the dendrons, and the dendron/solvent interactions, the envelope of these macromolecules would be a

cylinder.⁵ We report here two different approaches into poly(*p*-phenylene)s (PPP) whose backbones are densely packed with dendrons of generations one to three. The first starts from functionalized PPPs as polymeric cores whose functional groups are used to anchor dendrons; the second uses benzene derived monomers which already carry dendrons and which are then transferred into the corresponding PPP by some cleanly proceeding step-growth polymerization. The polymers are synthesized using the Suzuki polycondensation,⁶ the dendrons are attached either by using the Williamson ether synthesis or urethane formation, and the dendrons used are of the Fréchet-type.⁴

Results and Discussion

In the first orienting experiments toward cylindrically shaped dendronized polymers, Fréchet-type dendrons of the first (**1a**) and second generation (**2a**) were attached to the hydroxy anchor groups of PPP **4a** in the presence of sodium hydride as base (Chart 1).⁷ Whereas the attachment of **1a** gave **4b** with a degree of coverage >95%, the coverage with **2a** in **4c** could not be driven beyond some 50–60%. In light of this finding, the third generation dendron **3a** was not even tried. In order to determine if this limitation was due to steric hindrance between the dendrons, single crystals of the second generation dendron **2c** were grown and its structure was solved by X-ray diffraction.^{8–11} Dendron **2c** attains a more or less flat structure in the crystal (Figure 1a) and fills the volume of a cylinder with a height of 4 Å and a diameter of approximately 27 Å to 40–45% (Figure 1b). The repeat unit of **4a** is approximately 12.5 Å long and carries two hydroxy anchor groups. It is reasonable to assume that the polymer, in spite of the hindered rotation about the phenyl/phenyl bond, can adopt conformations allowing for a maximum distance between these groups. The conversion of

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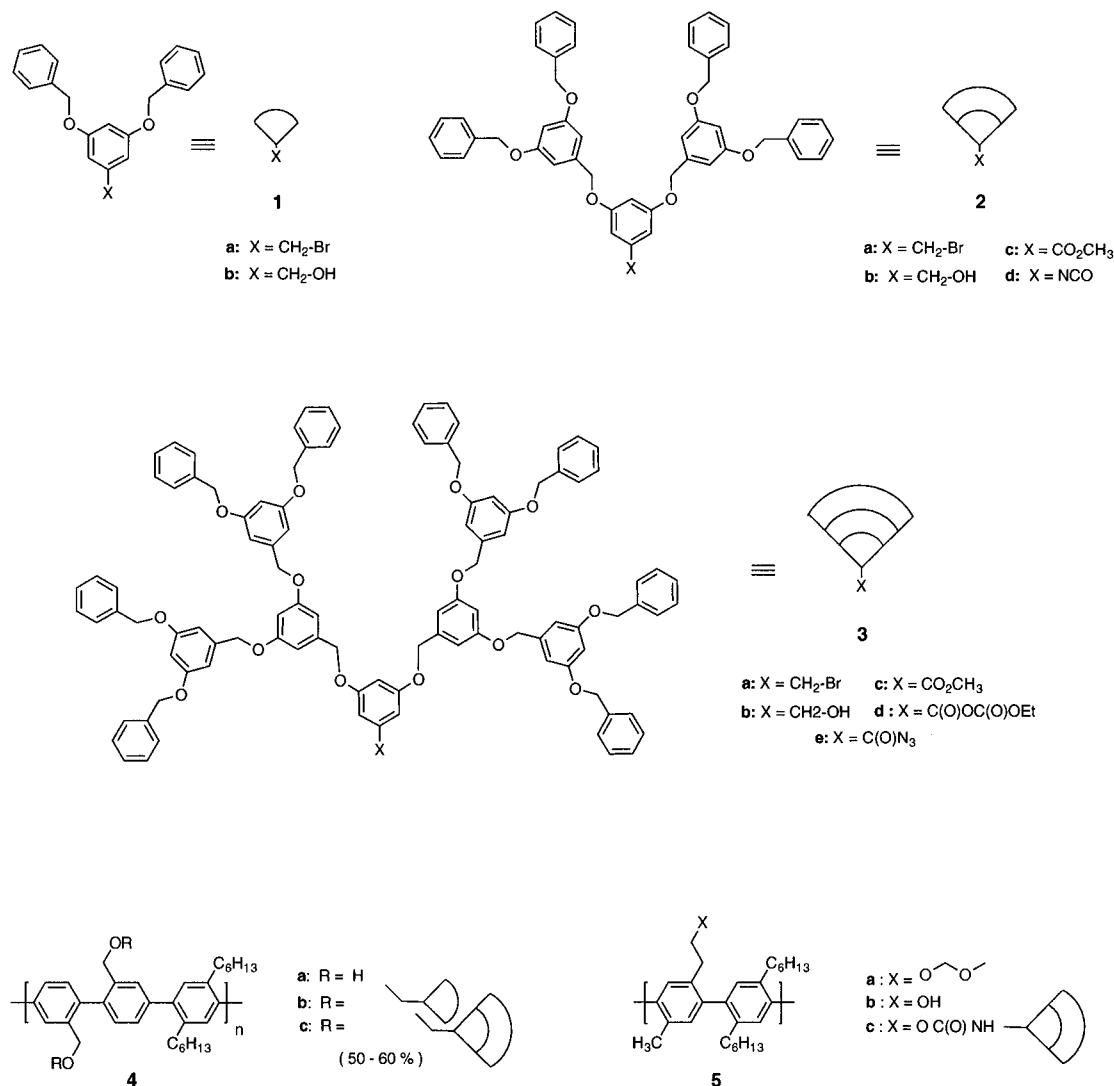
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(6) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. Schlüter, A.-D.; Wegner, G. *Acta Polym.* **1993**, *44*, 59.

(7) Schlüter, A.-D. *Am. Chem. Soc. Polym. Div., Polym. Prepr.* **1995**, *36* (1), 745.

(8) The author has deposited the atomic coordinates for this structure with the Cambridge Crystallographic Data Centre, and the coordinates may be obtained upon request from the Director, Cambridge Crystallographic Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

Chart 1



ortho-substituted oligophenylene atropic isomers into one another does not require activation energies unsurmountable at temperatures at which the attachment chemistry takes place. As can be seen from the cartoon of **4c** (Figure 1c), second generation dendrons are by far not voluminous enough to fill the space about the backbone. Even if one takes into account that the dendrons will certainly not remain planar once they are attached to the backbone and exposed to solvent, there is no steric reasoning which could explain more than some slowing of coupling of incoming dendrons by the ones already attached. Also the attachment of third generation dendrons seems to be within reach.

(9) Single crystals were grown from chloroform; 6466 unique X-ray diffraction data were collected on an Enraf-Nonius Turbo-CAD4 diffractometer with Ni-filtered Cu K α radiation from a rotating-anode generator ($\lambda = 1.542$, $\omega/2\theta$ scan mode, $2\theta_{\max} = 120^\circ$, nominal resolution $\lambda/2 \sin \theta_{\max} = 0.89$ Å, ψ scan absorption correction). The data were corrected for radiation damage (13% reduction in intensity of three reference reflections): space group triclinic, $P1$, $Z = 2$, $a = 8.0027(7)$, $b = 12.902(3)$, and $c = 20.857(5)$ Å, $\alpha = 72.45(2)^\circ$, $\beta = 88.09(1)^\circ$, $\gamma = 79.53(1)^\circ$, $V = 2018(3)$ Å³. The structure was determined by direct methods using program SIR 92 (ref 10) and refined with SHELX76 (anisotropic for non-hydrogen atoms) on the basis of 5074 reflections with $|F_o| > 1\sigma(F_o)$ (ref 11). H-Atoms bonded to the C-atoms were placed in their calculated positions with a fixed temperature factor of 0.04 Å². The crystallographic R -factor converged at 0.065.

(10) Altomare, A. et al. *J. Appl. Chem.* **1994**, *27*, 435.

(11) Sheldrick, G. M. SHELX76, Program for Crystal Structure Determination; University of Cambridge, U.K., 1976.

From this qualitative consideration it was concluded that the attachment chemistry was responsible for the failure to achieve a high coverage. In line with this interpretation is the recent finding that the hydroxy groups of polymer **5b** can in fact be completely covered with the isocyanate-carrying second generation dendron **2d** to give the urethane **5c**, although it should be noticed that the average distance between the anchor groups in **5b** is a little larger than that in **4a** and the hydroxies in **5b** are further apart from the backbone than in **4a** by one methylene group.¹² With this in mind experiments were devised (Scheme 1): (a) to reverse the course of the Williamson coupling by using a PPP with iodomethyl functions and dendrons of different generations with hydroxy functions at the focal point (reversed Williamson route), (b) to expand on the successful use of isocyanate dendrons, specifically by employing a third generation dendron and to test whether the reaction of this dendron and polymer **5b** can also be driven to completion (urethane route), (c) to complement experiments a and b by not only dendronizing polymers already prepared but also testing if dendronized monomers can be subjected to a PPP synthesis, thus shifting the dendronization step from after to before the polymerization (macromonomer route).

Reversed Williamson Route. Polymer **8b** could not be synthesized directly because of the incompatibility of the

(12) Karakaya, B.; Claussen, W.; Schäfer, A.; Lehmann, A.; Schlüter, A.-D. *Acta Polym.* **1996**, *47*, 79.

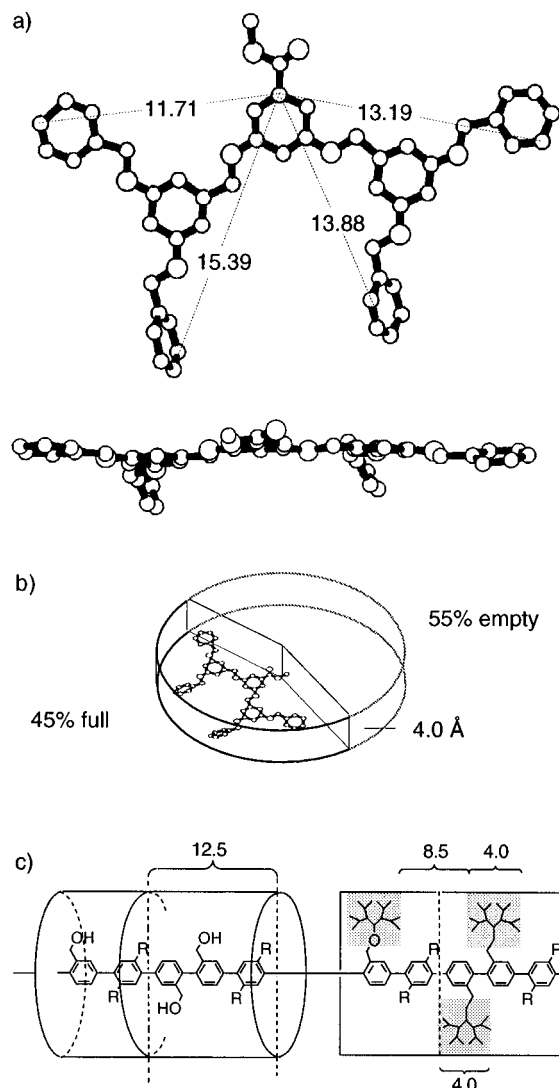


Figure 1. (a) Two perspectives of the crystal structure of second generation dendron **2c** (ORTEP), (b) illustration of the space demand of **2c**, and (c) oblique and sectional views of the cylindrical slices available for dendrons for polymer **4a** whose repeat unit is 12.5 Å long.

benzylic iodo function with the cross-coupling conditions. The protected precursor **8a** was therefore prepared first and subsequently transformed into **8b**. Polymer **8a** was obtained from the dibromo compound **6b** and diboronic acid **7**. Monomer **6b** was prepared on the 10 g scale by reacting *p*-methylbenzylic alcohol with bromine which gives the intermediate **6a**. This was then methanolyzed to **6b**. Monomer **7** which carries solubilizing hexyl chains has been a working horse in the synthesis of PPP derivatives and is easily available on the 20 g scale.¹³ The polycondensation of **6b** and **7** was done according to the standard procedure using the heterogeneous system water/1 M sodium carbonate and approximately 1.0 mol % of either palladium-tetrakis(triphenylphosphine) or palladium-tris(tri-*p*-tolylphosphine) as catalyst precursor.¹⁴ The degree of polymerization of **8a** could be adjusted to approximately $P_n = 25$ and $P_n = 80$ depending upon whether the catalyst precursor was used as purchased or in recrystallized form.¹⁵ The conversion of the benzylic substituent from methoxy to iodo

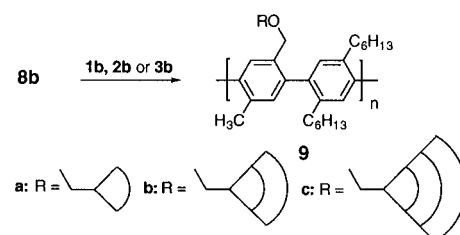
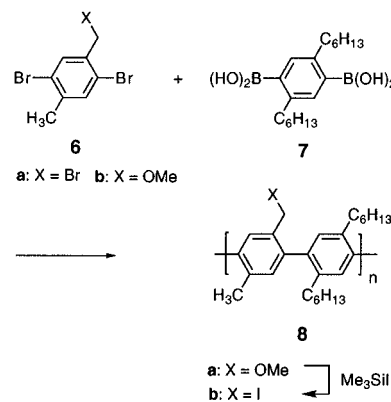
(13) Rehahn, M.; Schlüter, A.-D.; Wegner, G. *Makromol. Chem.* **1990**, *191*, 1991.

(14) Rehahn, M.; Schlüter, A.-D.; Wegner, G.; Feast, W. J. *Polymer* **1989**, *30*, 1060.

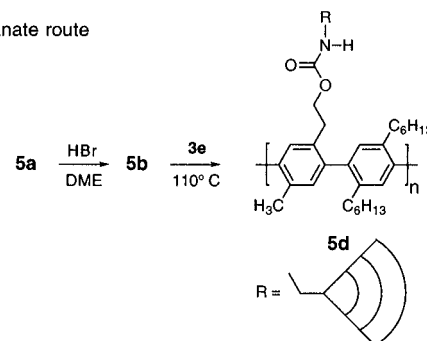
(15) This effect was also observed by Vanhee, S.; Rulkens, R.; Lehmann, U.; Rosenauer, C.; Schulze, M.; Köhler, W.; Wegner, G. *Macromolecules* **1996**, *29*, 5136.

Scheme 1

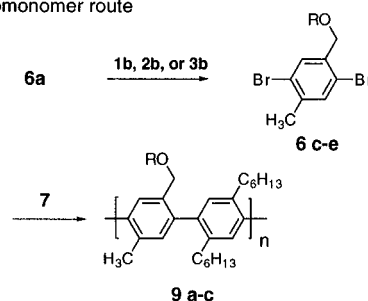
a) Reversed Williamson



b) Isocyanate route



(c) Macromonomer route



was done by reacting a solution of **8a** in chloroform with an excess of trimethyliodosilane (TMSI), which has been shown to cleanly replace certain methoxy by iodo functions.¹⁶ Standard work-up furnished polymer **8b** in virtually 100% yield regardless of its molecular weight. As can be seen from a comparison of the ¹H-NMR spectra of **8a** and **8b** (not shown) the methoxy signal of **8a** ($P_n = 25$) at $\delta = 3.3$ ppm has disappeared in the spectrum of **8b** to the advantage of a signal at $\delta = 4.1$ – 4.7 ppm which is assigned to the iodomethyl group. The line shape of this new signal presumably indicates the existence of

(16) Olah, G.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *J. Org. Chem.* **1979**, *44*, 1247. Rehahn, M.; Rau, I. U. *Makromol. Chem.* **1993**, *194*, 2225. Rehahn, M.; Rau, I. U. *Polymer* **1993**, *34*, 2889.

atropic isomers, a typical phenomenon for substituted oligo- and polyphenylenes.¹⁷ Even for **8a** ($P_n = 80$) this conversion proceeds with nearly 100%. The structural proof for **8a** and **8b** rests also upon the ¹³C NMR spectra as well as the data from elemental analysis.

For the dendronization experiments the shorter chain **8b** and a 3- to 5-fold excess of dendrons **1b**, **2b**, and **3b** were used. On deprotonation of the dendrons with sodium hydride in THF, the solutions stayed homogeneous and polymer **8b** was added. The course of the dendronization was monitored by analytical gel permeation chromatography (GPC). After completion, excess dendron was removed either by reprecipitation (**9a**, **9b**) or by preparative GPC (**9c**). The degrees of coverage were determined by NMR integration comparing the signal of the benzylic positions in the interior of the attached dendrons at approximately $\delta = 4.90$ ppm (or alternatively the signal of the inner aromatic protons at $\delta = 6.50$ ppm) with the one of the methyl groups of the hexyl chains at $\delta = 0.80$ ppm, which served as internal standard. The following coverages were obtained: **9a** (100%), **9b** (100%), and **9c** (70%). Depending on which of the low-field signals was used, the coverages obtained differed by 0–5%. Compared with the initially described dendronization of polymer **4a**, reversal of the course of the Williamson coupling obviously led to an improvement. For the first time, a second generation dendron could be attached completely and a third generation dendron to approximately 70%. Nevertheless there are serious drawbacks with this method. First, none of the polymers **9** gave satisfactory data from elemental analysis. Even after repeated reprecipitation and extensive drying at elevated temperatures in high vacuum, the carbon and hydrogen data, although consistent with one another, did not sum up to 100% but only to approximately 95%. A possible explanation may be the inclusion of inorganics. Second, the dendronization did not proceed well with the higher molecular weight polymer **8b** ($P_n = 80$). At an early stage of the dendronization, the polymer turned into a gel-like mass, which was insoluble in THF, CHCl₃, and toluene, and could, therefore, not be characterized properly.

Urethane Route. The methoxymethyl (MOM)-protected polymer **5a** was prepared as reported.¹² Best results for its deprotection to give **5b** were obtained with hydrogen bromide in dimethoxyethane (DME). Relatively high dilution conditions are required to bring about complete deprotection. When **5a** was used in less than roughly 0.01 M solutions, the MOM group was completely removed. If, however, the same reaction was done in a 0.1 molar solution, deprotection could not be driven beyond approximately 90% (for an illustration of the completeness of the deprotection, see ref 18). For the dendronization of **5b** with the third generation dendron **3e**, freshly freeze-dried polymer with a degree of polymerization $P_n = 82$ [GPC referenced to polystyrene (PS) standard] was reacted with a 5.5-fold excess of the acid azide dendron in refluxing toluene. After completion of the dendronization, side products due to reaction of the intermediately formed isocyanate with remaining traces of water and its self-condensation to cyclic and linear oligomers¹⁹ were removed by preparative GPC. Polymer **5d** was obtained as colorless material on the 200 mg scale. From a comparison of the intensities of the ¹H-NMR signals of all

Table 1. GPC Data of Polymers **5a–c**^a

polymer	M_n	P_n	M_w	P_w	D^b
5a	23 500	56	58 700	139	2.5
5b	31 000	82	84 000	222	2.7
5c	53 500	27	190 000	96	3.6

^a All measurements in THF at 20 °C versus PS. ^b $D = M_w/M_n$.

Table 2. GPC Data of Polymers **9a–c**^a

polymer	M_n	P_n	M_w	P_w	D^b
9a	19 300	29	68 700	103	3.6
9b	20 700	19	57 900	53	2.8
9c	52 400	27	275 500	142	5.3

^a All measurements in THF at 20 °C versus PS. ^b $D = M_w/M_n$.

methylene groups of the attached dendrons with the signal of the internal methyl group standard (see above), a coverage of 91–92% was determined. Table 1 contains the molecular weights (GPC) of polymers **5a**, **5b**, and **5d** from one and the same sample of **5a** which had been carried through this sequence of transformations trying to avoid fractionation.

Macromonomer Route. A comprehensive series of experiments were done to couple monomers to the corresponding PPPs which, from the very beginning, carry dendrons of varying size (macromonomers). This approach has the advantage that the polymers obtained are necessarily completely covered by dendrons. From a synthetic point of view, however, it has the disadvantage that potential shielding of the coupling sites by overhanging parts of the dendrons might occur. This would slow cross-coupling and favor side-reactions such as deboronification which in turn lead to termination. Macromonomers **6c–e** were obtained by reacting the tribromide **6a** with dendrons **1b**, **2b**, and **3b** (Scheme 1c) which were used only in slight excess. This was found the best compromise between the highest achievable yield on the one hand and the difficulties encountered with recycling of unused dendrons on the other. After several purification steps, analytically pure, “condensation grade” macromonomers were obtained on the several gram scale in yields of 40–80%, with a tendency to lower values with increasing generation. All dendrons gave satisfactory data from elemental analysis. The results of the polycondensation are summarized in Table 2. The polymers were further characterized by ¹H- and ¹³C-NMR spectroscopy and elemental analysis, the data of which deviate only slightly from the calculated ones.

Brief Comment on the Molecular Weights. The molecular weights of all polymers described in this paper were determined by GPC referenced to PS. The correctness of the values given in Tables 1 and 2 depends strongly on the quality of PS as reference. Since it is not reasonable to assume that PS is a good reference for the densely packed polymers reported here, and since it is also not known with certainty if these polymers behave like normal polymers on the column (exclusion and not adsorption as the separating factor), GPC data should be treated with great care. To gain more insight into this matter, a sample of **5d** (Table 1) and one of **9c** (Table 2) were investigated with a combined light-scattering/GPC/viscosimetry apparatus. The results are as follows: **5d** $M_n = 140\,000$, $M_w = 340\,000$, $M_w/M_n = 2.5$; **9c** $M_n = 300\,000$, $M_w = 780\,000$, $M_w/M_n = 2.6$. Even though the preparation of the samples (waiting time before injection, slow or fast filtration, etc.) did not have a great influence on these data, aggregation cannot be excluded. The rather tempting translation of the surprisingly high molecular weights, (specifically that of **9c**) into repeat units, therefore, is not allowed in the present stage.

(17) See, e.g.: Katz, H. E. *J. Org. Chem.* **1987**, *52*, 3932.

(18) Schlüter, A.-D. In *Step-Growth Polymers for High-Performance Materials*; Hedrick, J. L., Labadie, J. W., Eds.; ACS Symposium Series 624; American Chemical Society: Washington, DC, 1996; p 145.

(19) For a comprehensive treatment of isocyanate chemistry, see: Richter, R. Ulrich, H. *Syntheses and Preparative Applications of Isocyanates*. In *The Chemistry of Cyanates and Their Thio Derivatives*; (Patai, S., Ed.; Wiley: Chichester, 1977; p 619.

Conclusion

Dendronized PPPs can be obtained either by dendronizing already existing PPP backbones or by employing dendronized monomers in Suzuki cross-couplings. In the first approach, the best results are obtained when the attachment of the dendrons is done through urethane formation. This way even a third generation dendron can be attached to a PPP derivative with a number average degree of polymerization $P_n = 82$. The second approach is also successful despite the steric crowding of the macromonomers coupling site. The molecular weights achieved are at least as high as the ones of the first approach. This puts the most important advantage of the second approach nicely into the center of consideration, which is the fact that the degree of coverage is here inherently 100%. Thus, if the described hybrids of dendrimers and rigid-rod polymers actually attain cylindrical shape in solution (which still needs to be proved), their shape should undoubtedly be perfect.

Experimental Section

General Methods. Compounds **1**,⁴ **2a–c**,⁴ **2d**,¹² **3a–c**,⁴ **4**,^{3a} **5**,¹² and **7**¹⁴ were prepared according to literature procedures. 4-Methylbenzyl alcohol and trimethylsilyl iodide were purchased from Aldrich and used without further purification. Solvents were dried according to standard procedures. All reactions were carried out under nitrogen. The ¹H-NMR spectra of dendronized polymers were recorded with a repetition rate of 13 s and a sweep width of 20 ppm on a Bruker 500 MHz spectrometer in order to obtain reliable integrations. Signals that appeared because of traces of dirt in the probe head were automatically subtracted before integration. The molecular weight determinations were done using a Thermo Separation Products set-up with three DVB-mixed (DVB = divinylbenzene) bead columns, a H502B viscosimeter detector, and a Wyatt Dawn DSP laser photometer, coupled with an Optilab 903 interferometric refractometer. Complex molecular ion peaks in the mass spectra match perfectly with the calculated isotope pattern. Only the two most intense peaks are given (relative intensities).

1-Methyl-4-(bromomethylene)-2,5-dibromobenzene (6a). To a darkened solution of 4-methylbenzyl alcohol (24.4 g, 0.20 mol) in dichloromethane (20 mL) is dropped a solution of bromine (80 g, 0.50 mol) in the same solvent (10 mL) containing a few crystals of iodine. The resulting solution is refluxed for 1 d, another portion of bromine is added (20 g, 0.125 mol), and refluxing is continued for another 10 h. This solution is then poured into aqueous KOH (20%, 100 mL), and the phases are separated. The aqueous one is washed with methylene chloride (2 ×, 50 mL each), and the combined organic layers are dried over MgSO₄. After removal of the solvent, the residue is recrystallized from ethanol to give **6a** as colorless crystals. For **6a**: yield 46 g (78%); mp 72 °C; ¹H-NMR (270 MHz, CDCl₃) δ 2.34 (s, 3 H), 4.49 (s, 2 H), 7.40 (s, 1 H), 7.60 (s, 1 H); ¹³C-NMR (68 MHz, CDCl₃) δ 22.4, 32.1, 122.7, 123.8, 134.3, 134.8, 136.0, 140.2; MS (EI) *m/z* 342 (12.5), 344 (12.3). Anal. Calcd. for C₉H₁₀Br₂O (342.855): C, 28.03; H, 2.06. Found: C, 28.03; H, 2.06.

1-Methyl-4-(methoxymethylene)-2,5-dibromobenzene (6b). To a suspension of NaH (8.8 g, 0.35 mol) in dry THF (200 mL) is dropped methanol (10 g, 0.33 mol), the resulting mixture is stirred for 2 h at 20 °C before it is cooled to 0 °C and a solution of **6a** (17.1 g, 0.05 mol) in dry THF is added. After 12 h, the reaction is quenched with water and the layers are separated. The aqueous layer is washed with diethyl ether (2 ×), and the combined organic layers are dried over MgSO₄. After removal of the solvent, the oily residue is distilled through a 10 cm Vigreux column in high vacuum to give **6b** as a colorless liquid: yield 13.2 g (90%); bp 85 °C (0.001 mbar); ¹H-NMR (270 MHz, CDCl₃) δ 2.31 (s, 3H), 3.42 (s, 2H), 4.42 (s, 2H), 7.35 (s, 1H), 7.57 (s, 1H); ¹³C-NMR (68 MHz, CDCl₃) δ 22.2, 58.5, 72.9, 120.6, 123.8, 132.1, 133.9, 136.4, 138.5; HRMS calcd for C₉H₁₀Br₂O, *m/z* 291.9099, found 291.9093. Anal. Calcd. for C₉H₁₀Br₂O (293.985): C, 36.77; H, 3.43. Found: C, 36.40; H, 3.25.

[3,5-Bis(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)]-benzoyl azide (3e). To a cooled suspension of **3** (X = CO₂H) (3.6 g, 2.2 mmol) in acetone (150 mL) is added triethylamine (0.42 mL, 3.0

mmol) and chloroformic acid ethyl ester (0.29 mL, 3.0 mmol). This mixture is stirred for 1 h at 0 °C before an aqueous solution of sodium azide (1.24 g, 20 mmol) is added. The resulting suspension is stirred for 10 h, ice-water is added, and the mixture is extracted (3 ×) with dichloromethane. The combined organic layers are dried over MgSO₄, the solvent is removed at 0 °C in vacuum, and the residue is chromatographed through basic alumoxide (eluent hexane/acidic acid ethyl ester = 4:1). The product is freeze-dried (benzene) to give **3e** as white powder: yield 2.40 g (65%); ¹H-NMR (270 MHz, CDCl₃) δ 5.05 (m, 28 H), 6.65 (s, 8 H), 6.24 (m, 12 H), 6.90 (s, 1 H), 7.28–7.6 (m, 40 H); ¹³C-NMR (68 MHz, CDCl₃) δ 70.0, 101.5, 101.6, 106.3, 108.1, 108.3, 127.9, 128.5, 132.4, 136.7, 138.6, 139.1, 159.1, 160.1, 172. Anal. Calcd. for C₁₀₅H₈₉N₃O₁₅ (1632.869): C, 77.24.13; H, 5.49; N, 2.57. Found: C, 77.15; H, 5.60; N, 2.22.

Poly{2,5-dihexyl-1'-methyl-2'-[(((3,5-bis(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)]amino)carbonyloxy)ethyl]biphen-4,4'-diyl} (5d). To a refluxing solution of polymer **5b** (100 mg, 0.26 mmol) in dry toluene is added a solution of **3e** (1.38 g, 1.43 mmol) in dry toluene (20 mL), and refluxing is continued for 12 h when the reaction is quenched with water. The aqueous layer is washed with toluene (50 mL), and the combined organic layers are dried over MgSO₄. After removal of the solvent, the residue is separated into low molecular weight side products and the polymer by preparative GPC using THF as eluent. Polymer **5d** is then precipitated into ethanol and freeze-dried (benzene) to give a colorless material: yield 310 mg (59%); ¹H-NMR (500 MHz, CDCl₃) δ 0.84 (s, 6 H), 1.20 (s, 12 H), 1.46 (s, 4 H), 2.20 (s, 2 H), 1.47 (s, 4 H), 2.17 (s, 3 H), 2.46 (s, 4 H), 4.19 (s, 2 H), 4.92 (m, 28 H), 6.25 (m, 1 H), 6.57 (m, 21 H), 7.31 (m, 44 H); ¹³C-NMR (63 MHz, CDCl₃) δ 14.0, 19.7, 22.5, 29.0, 31.0, 31.5, 32.9, 65.4, 70.0, 97.9, 101.6, 106.4, 127.5, 127.9, 128.5, 130.2, 133.9, 136.8, 137.6, 139.2, 139.8, 153.1, 160.0. Anal. Calcd. for C₁₃₂H₁₂₇N₁O₁₆ (1983.48): C 79.93; H 6.45. Found: C 80.23; H 6.50.

Poly[2,5-dihexyl-2'-(methoxymethyl)-5'-methylbiphen-4,4'-diyl] (8a). To the two-phase system of 1 M Na₂CO₃ (100 mL) and toluene (30 mL) are added the monomers **6b** (524 mg, 1.8 mmol) and **7** (609 mg, 1.82 mmol). After careful degassing tris[tri(*p*-tolyl)phosphine]-palladium(0) (24 mg, 1.3 mol %) is added to this mixture which is then refluxed for 48 h. Sometimes the precipitation of metallic Pd is observed. The aqueous phase is washed with toluene (50 mL), and the combined organic layers are dried over MgSO₄. The organic layer is reduced to approximately 10 mL and then poured into MeOH (300 mL). The precipitate formed is recovered by centrifugation, and the procedure is repeated. Freeze-drying (benzene) affords polymer **8a** as fibrous material: yield 640 mg (94%); ¹H-NMR (270 MHz, CDCl₃) δ 0.82 (s, 6 H), 1.22 (s, 12 H), 1.46 (s, 4 H), 2.21 (s, 3 H), 2.43 (s, 4 H), 3.30 (s, 3 H), 4.28 (s, 2 H), 6.8–7.8 (m, 4 H); ¹³C-NMR (63 MHz, CDCl₃) δ 14.1, 20.0, 22.6, 29.2, 30.9, 31.6, 32.9, 35.5, 129.0, 130.1, 131.8, 133.8, 135.7, 137.7, 138.6, 139.6, 141.1. Anal. Calcd. for C₂₇H₃₈O (378.603): C, 85.66; H, 10.12. Found: C, 84.73; H, 9.75. For molecular weights, see text.

Poly[2,5-dihexyl-3'-(iodomethyl)-6'-methylbiphen-4,4'-diyl] (8b). To a solution of polymer **8a** (0.60 g, 1.6 mmol) in dry chloroform (50 mL) is added a solution of trimethylsilyl iodide (TMSI) (1.6 g, 8.0 mmol), and the mixture is refluxed for 24 h. The solvent (50 mL) is then removed, and refluxing is continued for another 24 h. The polymer is precipitated by pouring the cooled solution into MeOH (300 mL). Repetition of this procedure and freeze-drying (benzene) affords polymer **8b** as a colorless fibrous material: yield 648 mg (85%); ¹H-NMR (270 MHz, CDCl₃) δ 0.82 (s, 6 H), 1.23 (s, 12 H), 1.52 (s, 4 H), 2.20 (s, 3 H), 2.46 (s, 4 H), 4.00–4.80 (s, 2 H), 7.00–7.80 (m, 4 H); ¹³C-NMR (68 MHz, CDCl₃) δ 5.4, 19.8, 22.5, 29.1, 30.8, 31.6, 32.9, 35.5, 58.2, 72.2, 129.4, 130.1, 131.2, 133.1, 134.7, 137.5, 138.7, 139.6, 140.5. Anal. Calcd. for C₂₆H₃₅I (474.474): C, 65.82; H, 7.44. Found: C, 65.56; H, 7.32.

General Procedure for the Dendronization of Polymer 8b with Dendrons 1b, 2b, and 3b. To a suspension of NaH (for **1b** and **2b** 48 mg, 1.92 mmol; for **3b** 0.131 mg, 5.25 mmol) in THF (100 mL) is added the respective dendron (**1b** 0.20 g, 0.64 mmol; **2b** 0.47 g, 0.64; **3b** 1.67 g, 1.05 mmol), and after 12 h at 20 °C, the solution is decanted. A solution of polymer **8b** (100 mg, 0.21 mmol) in dry THF (15 mL) is then added dropwise. The mixture is stirred at 20 °C until it turns opaque and then refluxed for 24 h. After the reaction is quenched

with water, the phases are separated and the organic layer is dried over MgSO_4 . The solution is concentrated to 10 mL and poured into MeOH (300 mL). The precipitate formed is collected by centrifugation, redissolved in toluene, and precipitated into MeOH. This procedure is repeated until all excess dendron is removed (analytical GPC). For **9c** (70% coverage), excess dendron is removed by preparative GPC using THF as eluent. All polymers are freeze-dried (benzene). Yields: **9a** (129 mg, 92%), **9b** (214 mg, 94%), and **9c** (187 mg, 46%).

General Procedure for the Synthesis of Macromonomers 6c–6e. To a suspension of NaH (0.125 g, 5.0 mmol) in THF (150 mL) is added the respective dendron **1b**, **2b**, or **3b** (4.4 mmol), and the mixture is stirred for 12 h. Then a solution of **6a** (1.0 g, 2.91 mmol) in THF (10 mL) is added, and stirring is continued at 20 °C for 12 h. After the reaction is quenched with water, the phases are separated and the aqueous layer is extracted with dichloromethane (2×). The combined organic layers are dried over MgSO_4 . After removal of the solvent, the residue is chromatographed through basic alumoxide using hexane/acidic acid ethyl ester (4:1) as eluent. The raw product is recrystallized from the same solvents mixture to afford **6c**, **6d**, and **6e**, respectively, as colorless amorphous powders. Monomer **6e** can be freeze-dried (benzene).

1-Methyl-4-[(3,5-bis(benzyloxy)benzyloxy)methyl]-2,5-dibromobenzene (6c): yield 1.35 g (79%); mp 68 °C; $^1\text{H-NMR}$ (270 MHz, CDCl_3) δ 2.41 (s, 3 H), 4.53 (s, 2 H), 4.59 (s, 2 H), 5.09 (m, 4 H), 6.62 (s, 1 H), 6.77 (s, 2 H), 7.3–7.5 (m, 11 H), 7.71 (s, 1 H); $^{13}\text{C-NMR}$ (68 MHz, CDCl_3) δ 22.3, 69.9, 70.6, 72.6, 101.4, 106.5, 120.9, 123.8, 127.4, 127.8, 128.5, 132.4, 134.0, 136.7, 138.6, 140.2, 160; MS (EI) m/z 582 (1.4), 584 (0.6). Anal. Calcd. for $\text{C}_{29}\text{H}_{26}\text{Br}_2\text{O}_3$ (582.331): C, 59.81; H, 4.50. Found: C, 59.57; H, 4.46.

1-Methyl-4-[(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)methyl]-2,5-dibromobenzene (6d): yield 1.89 g (65%); mp 92 °C; $^1\text{H-NMR}$ (270 MHz, CDCl_3) δ 2.34 (s, 3 H), 4.52 (s, 2 H), 4.57 (s, 2 H), 4.95 (s, 4 H), 5.02 (s, 8 H), 6.58 (s, 3 H), 6.65 (s, 2 H), 6.69 (s, 4 H), 7.2–7.5 (m, 21 H), 7.68 (s, 1 H); $^{13}\text{C-NMR}$ (68 MHz, CDCl_3) δ 22.3, 69.9, 70.0, 70.7, 72.7, 101.5, 106.3, 106.6, 121.0, 123.9, 127.5, 128.0, 128.5, 132.6, 134.1, 136.7, 138.7, 139.2, 140.2, 160.0, 160.1; MS(EI) m/z 1006 (0.3), 1007 (0.2). Anal. Calcd. for $\text{C}_{57}\text{H}_{50}\text{Br}_2\text{O}_7$ (1006.826): C, 68.00; H, 5.01. Found: C, 68.28; H, 5.08.

1-Methyl-4-[(3,5-bis(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)benzyloxy)methyl]-2,5-dibromobenzene (6e): yield 2.35 g (44%); mp 125 °C; $^1\text{H-NMR}$ (270 MHz, CDCl_3) δ 2.33 (s, 3 H), 4.51 (s, 2 H), 4.53 (s, 2 H), 4.97 (m, 12 H), 5.00 (m, 16 H), 6.57 (m, 9 H), 6.65 (s, 12 H), 7.2–7.5 (m, 41 H), 7.68 (s, 1 H); $^{13}\text{C-NMR}$ (68 MHz, CDCl_3) δ 22.2, 69.9, 70.0, 70.7, 72.6, 101.5, 106.3, 106.6, 121.0, 123.8, 127.5, 127.9, 128.5, 132.5, 134.1, 136.7, 138.7, 139.2, 140.3, 160.0, 160.1. Anal. Calcd. for $\text{C}_{113}\text{H}_{98}\text{Br}_2\text{O}_{15}$ (1855.816): C, 73.13; H, 5.32. Found: C, 72.98; H, 5.41.

Polycondensation of Macromonomers 6c–6e. These experiments were done in full analogy to the synthesis of **8a**. For molecular weights, see Table 2.

Poly{2,5-dihexyl-2'-[(3,5-bis(benzyloxy)benzyloxy)methyl]biphen-4,4'-diyl} (9a). Compound **6c** (870 mg, 1.50 mmol), **7** (507 mg, 1.52 mmol), and $\text{Pd}[\text{P}(p\text{-tol})_3]_3$ (19 mg, 1.2 mol %) were used. For **9a**: yield 894 mg (90%); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 0.84 (s, 6 H), 1.34 (s, 12 H), 1.50 (s, 4 H), 2.16 (s, 3 H), 2.46 (m, 4 H), 4.38 (s, 4 H), 4.95 (m, 4 H), 6.54 (m, 3 H), 7.30 (m, 14 H); $^{13}\text{C-NMR}$ (68 MHz, CDCl_3) δ 14.0, 19.8, 22.5, 29.1, 31.0, 31.5, 32.6, 70.0, 72.3, 101.1, 106.3, 127.5, 127.9, 128.5, 130.2, 131.3, 133.1, 136.9, 137.4, 139.8, 141.1, 159.4. Anal. Calcd. for $\text{C}_{47}\text{H}_{54}\text{O}_3$ (666.953): C, 84.52; H, 8.16. Found: C, 83.78; H, 8.04.

Poly{2,5-dihexyl-1'-methyl-2'-[(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)methyl]biphen-4,4'-diyl} (9b). Compound **6d** (1.00 g, 0.99 mmol), **7** (336.8 mg, 1.005 mmol), and $\text{Pd}[\text{P}(p\text{-Tol})_3]_3$ (12 mg, 1.2 mol %) were used. For **9b**: yield 968 mg (89%); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 0.70 (s, 6 H), 1.12 (s, 12 H), 1.36 (s, 4 H), 2.05 (s, 3 H), 2.35 (s, 4 H), 4.30 (s, 4 H), 4.83 (m, 12 H), 6.51 (m, 9 H), 7.30 (m, 24 H); $^{13}\text{C-NMR}$ (68 MHz, CDCl_3) δ 14.0, 19.9, 22.5, 29.1, 30.8, 31.5, 32.8, 70.0, 72.4, 101.0, 101.5, 106.3, 127.5, 127.9, 128.2, 130.2, 131.3, 133.1, 136.9, 137.4, 139.8, 141.1, 159.8, 160.1. Anal. Calcd. for $\text{C}_{75}\text{H}_{78}\text{O}_7$ (1091.453): C, 82.54; H, 7.20. Found: C, 82.08; H, 7.20.

Poly{2,5-dihexyl-1'-methyl-2'-[(3,5-bis(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)benzyloxy)methyl]biphen-4,4'-diyl} (9c). Compound **6e** (1.87 g, 1.01 mmol), **7** (342 mg, 1.03 mmol), and $\text{Pd}[\text{P}(p\text{-Tol})_3]_3$ (12 mg, 1.1 mol %) were used. For **9c**: yield 1.88 g (96%); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 0.80 (s, 6 H), 1.15 (s, 12 H), 1.43 (s, 4 H), 2.14 (s, 3 H), 2.43 (s, 4 H), 4.39 (s, 4 H), 4.88 (m, 28 H), 6.62 (m, 21 H), 7.31 (m, 44 H); $^{13}\text{C-NMR}$ (68 MHz, CDCl_3) δ 14.1, 19.8, 22.5, 29.0, 31.5, 32.7, 69.9, 72.5, 101.6, 106.3, 127.5, 127.9, 128.5, 131.4, 136.8, 137.5, 139.2, 141.2, 160.0. Anal. Calcd. for $\text{C}_{75}\text{H}_{78}\text{O}_7$ (1940.456): C 81.09; H 6.55. Found: C 80.23; H 6.50.

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Supporting Information Available: Crystallographic details for **2c** (12 pages). See any current masthead page for ordering and Internet access instructions.

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