Entering a New Level of Use for Suzuki Cross-Coupling: Poly(*para*-phenylene)s with Fourth-Generation Dendrons

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Abstract: Three different synthetic routes to the fourth-generation (G4) macromonomers **4**, **6**, and **9** for Suzuki polycondensation (SPC) are described and compared in their efficiency. Monomer **9** was selected the best as judged by the number and feasibility of synthetic steps and purification behavior and could be prepared in a 15 g scale. SPC of the monomers **4**, **6**, and **9** gave the novel poly(*para*-phenylene)s **17**, **18**, and **19** with pendant G4 dendrons at every other repeat unit. SPC was optimized for **9** and the diboronic acid ester counterpart **16** which led to polymer **19** with a molecular weight of up to $M_n = 76000$, $M_w = 639000$ (GPC versus polystyrene). High molecular weight is most likely to be obtained for the attempted stoichiometry **9**:**16** = 1.000:(0.995 – 1.005).

Keywords: dendrimers · palladium · polymers · polymerizations

Introduction

In recent years particular interest arose in dendrimers which do not have the commonly observed spherical,[1] but rather cylindrical shape.[2] These macromolecules were synthesized by divergent and convergent strategies and, most importantly, by the macromonomer route in which dendronized monomers are polymerized.[2] This route avoids defective dendrons or incomplete coverage, problems that are encountered in other strategies. It is not surprising, therefore, that several groups have put a lot of effort into the macromonomer route.[3] Practically all reported examples use monomers with first- and second-generation dendrons (G1, G2). Occasionally spacers are introduced between dendron and the polymerizable group in order to enable polymerization. A Suzuki-type[3a,b] and styrene-based macromonomer[3c] are the only two cases where G3 macromonomers were successfully polymerized. Recently we communicated the synthesis of a G4 Suzuki (AA type) monomer and initial results of its Suzuki polycondensation (SPC) which gave oligomeric material.[4, 5] Most importantly a small fraction of a polymer with $P_n = 45$ (GPC versus PS) was isolated. This seemed to indicate that the polymerization is intrinsically possible and that there may be a reason besides steric hindrance why only oligomers were formed. We reasoned that the considerable molecular weight difference between the two monomers, a dendronized dibromobenzene with approximately 3500 g mol^{-1} and a benzene diboronic acid ester with approximately 250 g mol^{-1}, together with the relatively small scale in which these experiments had to be done due to lack of sufficient access to monomer, made it difficult to meet the correct stoichiometry. Additionally, the amount in which the dendronized macromonomer can be prepared at a reasonable effort/yield proportion (1 g) did not allow an extended series of optimization experiments.

In this paper we report the full details of the reported results and on two practical syntheses of novel G4 SPC macromonomers, one of which was scaled up to 15 g per run. With this latter monomer a series of polymerization experiments was performed in order to investigate whether or not SPC can cope with the considerable steric hindrance imparted by it.

Results and Discussion

Monomer synthesis: Scheme 1 shows the synthetic routes (A – C) to the G4 monomers **4**, **6**, and **9** which all start from tribromide **1.** This compound was selected as starting material because it can be prepared on a 100 g scale and we have much experience with it in our laboratory.[3a]

Route A: The synthesis of monomer **4** was already outlined in a communication.[5] Herein the full account is given. The sequence to **4** passes through tetrabromide **2** which has two sterically unhindered benzylic functions. This way the substitution at these positions with large dendrons is not addi-

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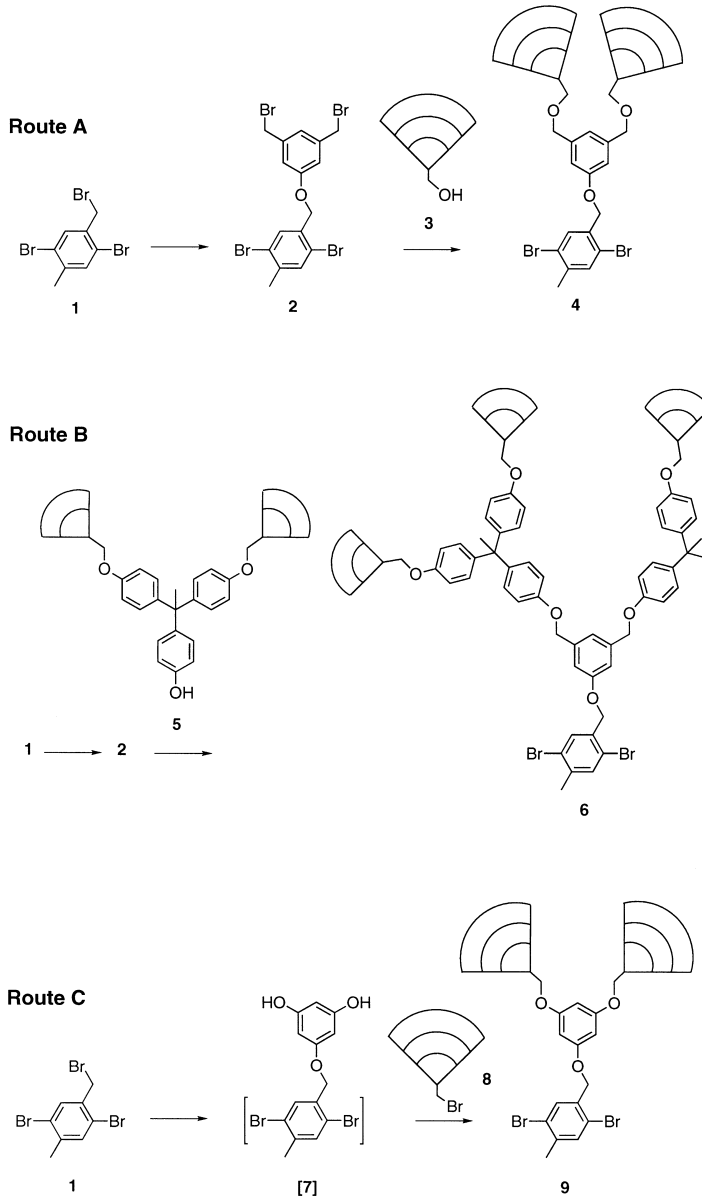
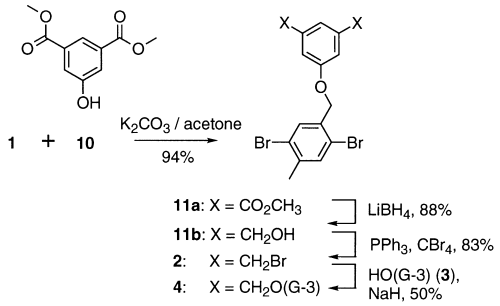


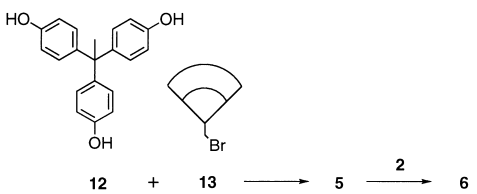
Scheme 1. Optimized routes for the synthesis of macromonomer **4**, **6**, and **9**.

tionally hampered by steric factors as in the case of **1** where an *ortho*-bromo substituent is in close proximity to the benzylic function. Coupling of compound **1** with the commercially available phenol diester **10** gave dibromo diester **11a** whose borohydride reduction followed by Appel bromination yielded **2** on the 10 g scale (Scheme 2). Reaction of **2** with G3 alcohol **3** was done under standard Williamson etherification conditions using THF or DME or a mixture of both as solvent and sodium hydride as base. The purification of **4** was somewhat tedious. Repeated column chromatography on silica gel left a few percent of unidentified, low molecular weight impurities (determined by analytical GPC). Analytically pure **4** was obtained on the 2 g scale by first passing it through a normal column and second applying preparative GPC using THF as eluent. Occasionally, impurities were brought into the system by the large amounts of solvents required for the latter separation and had to be removed by one further column chromatography step. An additional complication was the sensitivity of the G4 monomer **4** to silica gel. If a separation took longer than a day, partial decompostion of the dendron was occasionally observed.

Route B: This route utilizes the high efficiency of the coupling between phenols and benzylic bromides, which can even cope with steric hindrance.[6] Dendron **5** with its phenolic focal point is attached to **2** by Williamson etherification. The seemingly easiest way to this dendron, which is to attach two equivalents of G2 bromide to 1,3,5-trihydroxybenzene, was not used, because carbon alkylation reactions could not be easily suppressed. The commercially available 2,2,2-tris(4-hydroxyphenyl)ethane (**12**) was used instead (Scheme 3). G3 dendron **5** was synthesized by statistically reacting G2 bromide with **12**. A yield of 31 % was obtained when the two components were used in the ratio 2.2:1. Dendron **5** was prepared on the 2.5 g scale. Coupling of **5** with **2** after column chromatography gave G4 monomer **6** in 84 % yield. Monomer **6** was freeze-dried from benzene to



Scheme 2. Synthesis of macromonomer **4**.



Scheme 3. Synthesis of macromonomer **6**.

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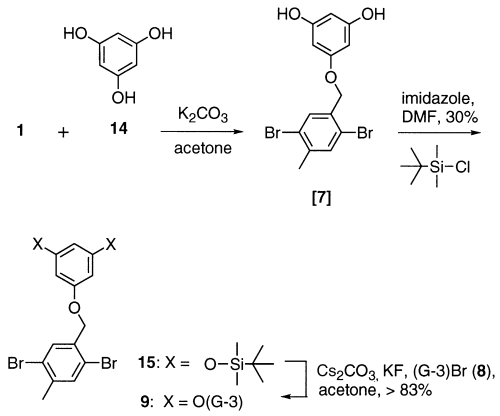
remove traces of solvent. Its structure was established by the fully assigned NMR spectra and correct data from elemental analysis. The GPC chromatogram shows only one monomodal and symmetrical peak with a polydispersity $M_w/M_n < 1.01$.

Route C: Route C reverses the order of Williamson ether synthesis of routes A and B. Compound **7** with its two phenoxy groups replaces the tetrabromide **2**. Addition of the G3 benzylic bromide **8** gives the G4 monomer **9**. Trihydroxybenzene **14** was selected as starting material for **7** because of its low price (Schemes 1, 4). Reaction of **14** (10 equiv) with compound **1** under standard K_2CO_3/acetone conditions gave the expected mixture of the desired compound **7** and side products.[7] Aryl ether **7** was not directly purified but rather transferred into its silyl derivative **15** by treatment of the crude compound containing between 60–80% of the desired material with dimethyl(1,1-dimethylethyl)silyl-chloride. Subsequent purification by silica gel column chromatography gave compound **15** in 30% yield from **1**. The fully assigned NMR spectra and correct data for the elemental analysis proved the proposed structure. Reaction of G3 bromide **8** with compound **15** in presence of Cs_2CO_3/KF/acetone gave G4 dendritic monomer **9** in one step, whereby KF was used to remove the silyl protecting groups in situ. Pure **9** was obtained by normal silica gel column chromatography in yields of 83–92% on the 15 g scale. 500 MHz NMR spectra, elemental analysis, and the monomodal, symmetrical GPC elution curve with a polydispersity $M_w/M_n < 1.01$ are in agreement with the structure and indicate a purity > 98%.



Scheme 4. Synthesis of macromonomer **9**.

Comparison of Routes A–C

Route A: *Advantages*: Compound **2** and Fréchet-type dendron **3** are easy to prepare on the multi gram scale. *Disadvantages*: Dendron **3** carries a benzylic hydroxy group which is not optimal for the subsequent Williamson ether synthesis with compound **2** regarding satisfactory yields. Purification of monomer **4** requires preparative GPC which limits the accessible amount to 1–2 g.

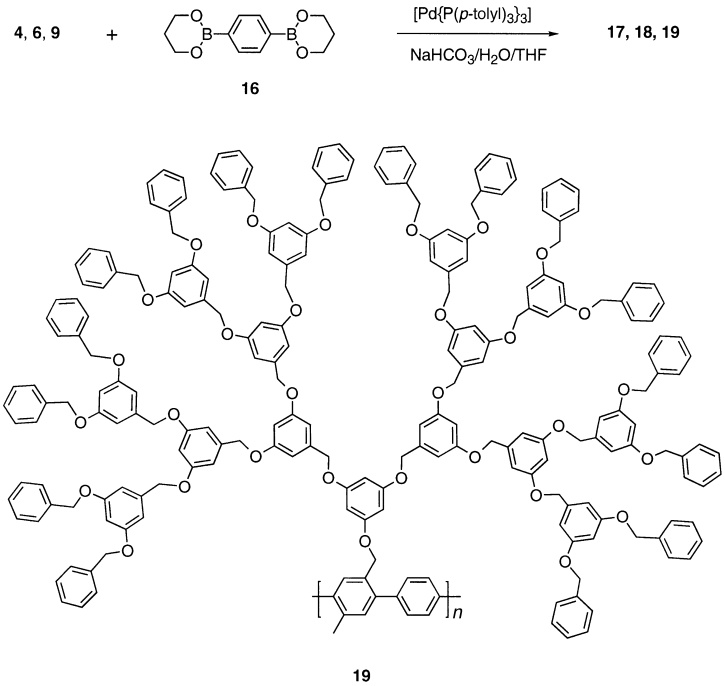
Route B: *Advantages*: Dendron **5** carries a phenolic group at focal point. It is accessible from commercially available **12** and the amply available Fréchet-type G2 bromide **13**. *Disadvantages*: None, under synthetic aspects. The G4 dendron in monomer **6** has a relatively large branching unit, however, which upon SPC will lead to somewhat less densely packed cylindrical dendrimers.

Route C: *Advantages*: Synthesis of key compound **15** requires two simple steps and purification is simple. 3–4 g of **15** can be obtained in a single reaction which will yield up to 15 g of monomer **9**. Purification of **9** by column chromatography is facile even if done on this scale. *Disadvantages*: Synthesis of **15** proceeds with 30% yield only. Because of the large amounts of side products the overall handling of **7** is somewhat difficult.

The emphasis in this work was therefore placed on **9** because this should give the most densely packed PPPs and in this regard was considered the most serious case to probe whether or not SPC can cope with the steric demand of G4 monomers.

Polymer Synthesis and Characterization

SPC is a useful method for the synthesis of well-defined, high molecular weight polyarylenes.[8] Cross coupling of aromatic dihalides with aryl diboronic acid esters is usually done in 2 M aqueous $NaHCO_3$ and THF with 0.6–1.5 mol-% $[Pd(PPh_3)_4]$ or $[Pd\{P(p\text{-tolyl})_3\}_3]$ as catalyst precursor.[9] Freshly prepared $[Pd\{P(p\text{-tolyl})_3\}_3]$ seems to be the superior choice of the two in many cases.[10] Some researchers prefer to use the boronic acid component in a slight excess due to slow deboronification.[11] SPCs were carried out with G4 monomers **4**, **6**, and **9**, and the boronic ester conterpart **16** to give polymers **17, 18**, and **19**, respectively (Scheme 5). The structures of **17** and **18** are not shown. The results are summarized in Table 1. All three monomers are soluble in THF and the standard conditions were applied unchanged. They were used in analytically and NMR spectroscopically pure form. The largest series of



Scheme 5. Synthesis of polymer **19**.

Table 1. Conditions and molecular weights of polymer **17**, **18**, and **19** prepared.

Entry	Monomer	Ratio to **16**	mol-% of [Pd{(*p*-tolyl)$_3$}$_3$]	Polymer obtained [mg, %]	M_n [kDa]	P_n	M_w [kDa]	P_w	PD
1[a]	**4**	1.000:1.005	2.5[b]	**17** (260, 92)	21	6	51	15	2.4
2[a]	**4**	1.000:1.005	1.07[b]	**17** (740, 96)	24	7	49	14	2.0
3[a]	**4**	1.000:1.005	0.60[b]	**17** (980, 94)	16	5	18	8	1.7
4	**6**	1.000:1.005	1.61	**18** (530, 94)	24	6	33	11	1.8
5	**6**	1.000:1.005	2.70	**18** (170, 91)	24	5	36	9	1.7
6	**9**	1.000:0.995	0.74	**19** (1080, 100)	41	12	88	25	2.1
7	**9**	1.000:0.995	0.43	**19** (880, 100)	39	12	97	28	2.5
8	**9**	1.000:1.000	1.04	**19** (880, 100)	89	25	442	125	5.0
9	**9**	1.000:1.000	0.78	**19** (880, 99)	54	15	149	43	2.8
10	**9**	1.000:1.005	2.27	**19** (570, 87)	32	9	71	21	2.2
11	**9**	1.000:1.005	0.71	**19** (710. 93)	33	10	75	22	2.3
12	**9**	1.000:1.005	0.56	**19** (950, 100)	76	22	639	182	8.4
13	**9**	1.000:1.005	0.95	**19** (810, 97)	29	8	69	20	2.4
14	**9**	1.000:1.010	0.38	**19** (830, 94)	42	12	106	30	2.5
15	**9**	1.000:1.010	1.21	**19** (1000, 100)	30	9	59	17	1.9
16	**9**	1.000:1.020	1.04	**19** (910, 94)	24	7	45	13	1.8

[a] See ref. [5]; [b] [Pd(PPh$_3$)$_4$] was used instead of [Pd{(*p*-tolyl)$_3$}$_3$].

experiments was performed with monomer **9** to furnish polymer **19**. These experiments are therefore described here in more detail. As is the case of monomers **4** and **6**, the molecular weight difference between **9** and the boronic ester counterpart **16** is considerable (**9**: 3540 g mol^{-1}; **16**: 246 g mol^{-1}). Consequently the polycondensations were run at or near the 1 g scale for **9** in order to be able to weigh in the lighter **16** with sufficient accuracy. To meet the 1:1 stoichiometry, 1 g of **9** required 69.5 mg of **16**. The amounts of catalyst precursor were in the range of 1–3 mg (0.4–1.2 mol-%). The mol ratios were systematically varied between **9**:**16** = 1.000:0.995 and 1.000:1.020 (entries 6–16) in order to find the optimum as there a) may always be some trace impurities and b) deboronification may play a role in this case of sterically hindered SPC. A detailed description of the procedure can be found in the Experimental Section.

The molecular weights of polymer **19**, determined by GPC against polystyrene standard, range between $24\,000 < M_n < 89\,000$ and $45\,000 < M_w < 639\,000$ which translates into $7 < P_n < 25$ and $13 < P_w < 182$ (Table 1). The elution curves are monomodal in most cases but show some shoulders for entries 8 and 12 where polydispersities are broad. From the comparison of GPC and small angle neutron scattering (SANS) data of various polymers with appendent G1, G2, and G3 dendrons it has been proven that GPC referenced to polystyrene considerably underestimates the actual molecular weights.[12, 3e] Factors between 1.5–4 were determined. It is, however, not obviously clear that similar factors also apply to the polymers with G4 groups reported here. At present no attempt is undertaken to extrapolate the actual molecular weights from the numbers of Table 1, although a program to determine the molecular weights of some samples by SANS has already been started.

Some conclusions can be drawn from entries 6–16: a) High molecular weight material can in fact be obtained (entries 6, 7, 8, 9, 12, 14), b) no straight correlation exists between monomer stoichiometry (presumed to have been realized) and molecular weight though most good results are observed for **9**:**16** = 1.000:(0.995–1.005), and c) variation of catalyst precursor to monomer ratio does not seem to have much influence. The data, however, reflect some irrationality which may mirror the still not completely overcome considerable experimental difficulty in matching the correct stoichiometry. It may well be that within the mentioned range high molecular weights were obtained more or less by accident. The molecular weights of polymers **17** and **18** obtained from monomers **4** and **6** (entries 1–5) were lower than for **19**. This is presumably not due to an intrinsic limitation but to an insufficient optimization of SPC caused by the limited availability of monomers **4** and **6**. The quantities prepared allowed only for 2–3 independent runs per monomer.

The polymers were characterized by their highly resolved, high-field ^{1}H- and ^{13}C-NMR spectra as well as by the data from combustion analysis which matched the calculated values very well (see Experimental Section). The proton chemical shifts of polymer **19** are shifted up-field as compared with monomer **9** by approximately $\Delta\delta = 0.1–0.25$ ppm. This qualitatively reflects the steric crowding in the dendritic layer around the backbone. Polymers **17** and **18** gave similar results. An attempt was made to determine the molecular weight of polymer **17** by NMR end group analysis and to correlate these data with GPC. This polymer was selected because its end groups are separated off the best from the main signals in the ^{1}H-NMR spectra. A sample of **17** (Table 1, entry 2) was separated by preparative GPC into three fractions: a) $M_n = 13\,000$ ($P_n = 4$), $M_w = 19\,000$ ($P_w = 5$), PD = 1.5, b) $M_n = 24\,000$ ($P_n = 7$), $M_w = 33\,000$ ($P_w = 10$), $PD = 1.4$, and c) $M_n = 66\,000$ ($P_n = 19$), $M_w = 87\,000$ ($P_w = 25$), PD = 1.3. A fourth fraction d) with $M_n = 170\,000$ ($P_n = 46$), $M_w = 234\,000$ ($P_w = 67$), PD = 1.4 was taken from ref. [5]. For all fractions 500 MHz NMR spectra were recorded to ensure that the integrals over all signals were fully consistent with the calculated number of protons. All end group signals appeared down-field from the corresponding main signals by approximately 0.1–0.25 ppm. They were identified as such by comparison with the signals of the monomer. The end group signals of the outermost methylene groups (position B^5) and the aromatic branching units (symmetrical Hs at those benzene rings which carry two O and one C substituent, position D^5) were separated best and therefore used for integration. The degree of polymerization

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obtained by this integration depended somewhat on which of the two end groups was compared with the respective main signal. The P_n (NMR) values were as follows (the first value refers to position D and the second to position B): fraction a) 19–25, b) 20–26, c) 34–42, and d) 38–52. These figures were calculated assuming that each end group signal is caused by one dendron which may or may not be the case. Comparing these values with those from GPC (see above) one observes a discrepancy which is significant even considering the uncertainty of the NMR values. Especially for the lower molecular weight fractions, GPC considerably underestimates the real molecular weight, which is qualitatively within the same limit with the comparison of GPC and SANS data for various dendronized polymers.[12] For fraction d) which contains high molecular weight material both methods of weight determination came to roughly comparable results. To further substantiate this point SANS measurements would be required.

Conclusion

G4 dendronized SPC-type macromonomers can be synthesized at a reasonable effort/yield ratio. Despite their sterically demanding, dendritic substituent these monomers undergo SPC which, after rigorous optimization, leads to high molecular weight material. Within extended series of experiments it was found that high molecular weight polymer **19** is most likely to be obtained for the stoichiometry range **9**:**16** = 1.000:(0.995–1.005). The highest molecular weight obtained for **19** was $M_n = 76000$, $M_w = 639000$. Though these values were obtained by GPC versus polystyrene and are therefore to be treated with care they clearly indicate the formation of high molecular weight material and, thus, show the unexpected potential of SPC to cope even with such excessively loaded monomers.

Experimental Section

Compounds **1**,[3a] **3**,[6] **4**,[5] **8**,[6] **16**,[9] and **17**[5] were prepared according to literature procedures. Compounds **10**, **12**, and **14** were purchased from Aldrich or Fluka. The catalyst precursor {Pd[P(*p*-tolyl)$_3$]$_3$} was prepared according to the literature[13] and preferentially used fresh or within 2 d at the longest when stored under nitrogen in a high quality glove box. Reactions were carried out under nitrogen and worked up according to standard procedure. NMR spectra were recorded on a Bruker AM 500 spectrometer. The molecular weight determinations were done using a Thermo Separation Products set up with three DVB-mixed (DVB = divinylbenzene) bead columns, a H520B viscometer detector, and a Wyatt Dawn DSP laser photometer, coupled with an Optilab 903 interferometric refractometer. Elemental analysis was done for monomers and polymers only.

General procedure A for synthesis of 5, **6**, **7** (see **15**), **and 11a**: A mixture of phenol, benzylic bromide, K_2CO_3, 18-crown-6, and acetone was refluxed for 24 h. The solvent was evaporated to dryness, the residue partioned between water and CH_2Cl_2, the organic layer separated, and the aqueous layer extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, and evaporated to dryness. The crude product was purified by silica gel column chromatography. The lower molecular weight compounds were recrystallized, and the higher molecular weight compounds freeze-dried.

4-{{1,1-Bis{4,4′-bis[3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyloxy}phenyl}-ethyl}phenol (5): See general procedure A: (G-2)Br **13** (8,6 g, 10.65 mmol), **12** (1.63 g, 5.32 mmol), K_2CO_3 (4.16 g, 30.0 mmol), 18-C-6 (10 mg), and acetone (150 mL) were used. The crude material was purified by silica gel chromatography eluting with CH_2Cl_2 gradually increasing to CH_2Cl_2/diethyl ether 5:1 to give **5** as a colorless solid (2.9 g, 31%). ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.42-7.29$ (m, 40H), 6.90 (AB system, 8H), 6.75 (AB system*, 4H; *the high field part of this AB system was superimposed by the signal at $\delta = 6.66$), 6.66, 6.65, 6.55, 6.52 (four sets of signals, 18H), 5.01 (s, 16H), 4.95 (s, 12H), 2.07 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta =$ 160.18, 160.05, 156.77, 153.47, 142.08, 141.94, 139.61, 139.24, 136.78, 129.81, 129.63, 128.57, 127.98, 127.54, 119.27, 114.54, 114.05, 106.44, 101.64, 101.56, 70.13, 70.01, 69.92, 50.64, 30.77; anal. calcd for $C_{118}H_{102}O_{15}$ (1760.1): C 80.52 H 5.84; found: C 80.08 H 5.75.

2,5-Dibromo-4-methyl-{3,5-bis{4-{1,1-bis{4,4′-bis[3,5-bis[3,5-bis(benzyloxy)-benzyloxy]benzyloxy}phenyl}ethyl}phenoxymethyl}phenoxymethyl}benzene (6): See general procedure A: Compound **5** (1.00 g, 0.568 mmol), **2** (0.14 g, 0.258 mmol), Cs_2CO_3 (0.326 g, 1.00 mmol), and acetone (50 mL) were used. The crude material was purified with silica gel chromatography eluting with CH_2Cl_2 and freeze-dried from benzene give **6** as a colorless amorphous solid (0.85 g, 84%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.69$ (s, 1H), 7.40–7.26 (m, 81H), 7.09 (s, 1H), 6.98 (s, 2H; this signal was superimposed to the lower field part of the AB system's peaks centered at $\delta = 6.91$), 6.91 (AB system, 24H), 5.00–4.93 (five sets of single peaks, 62H), 2.33 (s, 3H), 2.08 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 159.97$, 159.85, 156.59, 141.98, 141.89, 139.37, 139.02, 136.55, 129.51, 129.06, 128.45, 127.88, 127.44, 113.82, 106.19, 101.35, 69.91, 69.79, 69.47, 50.48; anal. calcd for $C_{252}H_{216}Br_2O_{31}$ (3900.3): C 77.60 H 5.58; found: C 77.12 H 5.50.

Dimethyl-5-(2,5-dibromo-4-methylbenzyloxy)-1,3-benzene dicarboxylate (11a): See general procedure A: Compound **1** (4.82 g, 14.1 mmol), **10** (3.15 g, 15.0 mmol), K_2CO_3 (3.5 g, 38.4 mmol), 18-crown-6 (10 mg), acetone (200 mL). The reaction mixture of the crude product was washed with aqueous KOH solution, water, and saturated NaCl solution before drying. The product was purified by column chromatography with CH_2Cl_2 (6.25 g, 94%). ^{1}H NMR ($CDCl_3$): $\delta = 8.31$ (s, 1H), 7.83 (s, 2H), 7.69 (s, 1H), 7.44 (s, 1H), 5.11 (s, 2H), 3.93 (s, 6H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 165.97$, 158.29, 139.62, 134.54, 134.37, 132.42, 131.95, 124.06, 123.62, 120.78, 120.08, 118.56, 69.00, 52.45, 22.41.

2,5-Dibromo-1-methyl-4-[3,5-bis[3,5-bis[3,5-bis[3,5-bis(benzyloxy)benzyl-oxy]benzyloxy]benzyloxy]benzyloxymethyl]phenoxymethyl]benzene (4): G3-OH (2.39 g, 1.5 mmol) was added to a suspension of NaH (43.3 mg, 1.8 mmol) in dimethoxyethane (DME) (300 mL). After 12 h at rt, a solution of **2** (379 mg, 0.7 mmol) was added dropwise. The mixture was stirred for 2 d at rt, and then refluxed for 1 d. The reaction was quenched with a small amount of water, and the solvent was evaporated to dryness. The residue was partioned between water and CH_2Cl_2, the organic phase separated, and the aqueous one extracted with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$, and evaporated to dryness. Crude **4** was dissolved in benzene and freeze-dried before silica gel column chromatography (CH_2Cl_2 as eluent), preparative GPC (THF as eluent), and again silica gel column chromatography (CH_2Cl_2 as eluent). Monomer **4** was finally taken up into benzene and freeze-dried (1.25 g, 50%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.64$ (s, 1H), 7.37–7.26 (m, 91H), 6.97 (s, 1H), 6.90 (s, 2H), 6.63–6.47 (m, 42H), 4.96 (s, 32H), 4.89 (s, 24H), 4.47 (s, 4H), 4.43 (s, 4H), 2.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 160.04$, 159.93, 159.90, 158.53, 140.60, 140.08, 139.18, 139.11, 136.67, 135.24, 134.12, 132.18, 128.52, 128.30, 127.94, 127.68, 127.52, 127.27, 123.96, 120.50, 119.84, 113.16, 106.49, 106.33, 106.27, 101.45, 101.21, 72.09, 71.81, 69.95, 69.84, 68.45, 23.24; anal. calcd for $C_{226}H_{196}O_{31}Br_2$: C 76.08, H 5.54; found: C 75.98, H 5.71.

2,5-Dibromo-4-methyl-[3,5-bis[3,5-bis[3,5-bis[3,5-bis(benzyloxy)benzyl-oxy]benzyloxy]benzyloxy]benzyloxy]phenoxymethyl] benzene (9): A mixture of (G-3)Br **8** (2.82 g, 1.71 mmol), **15** (0.50 g, 0.81 mmol), KF (1 g, 17.2 mmol), Cs_2CO_3 (1 g, 3.1 mmol), and acetone (100 mL) was stirred and refluxed for 48 h. The solvent was evaporated to dryness, the residue was partioned between water and CH_2Cl_2. The organic layer was separated, the aqueous layer was extracted with CH_2Cl_2, and the combined organic phase was dried over $MgSO_4$ and then evaporated to dryness. The residue was purified by silica gel chromatography eluting with CH_2Cl_2, and freeze-dried from benzene to give pure **9** as white amorphous solid (12.59 g, 83%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.63$ (s, 1H), 7.38–7.27 (m, 81H), 6.64

(three overlapping signals, 28H), 6.53–6.52 (three partially overlapping signals, 14H), 6.23 (s, 1H), 6.21 (s, 2H), 4.96–4.84 (two sets of five overlapping signals, 64H), 2.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 160.39, 159.95, 159.86, 139.01, 136.56, 128.43, 127.86, 127.43, 106.16, 101.36, 69.87; anal. calcd for $C_{224}H_{192}Br_2O_{31}$ (3539.8): C 76.01 H 5.47; found: C 75.95 H 5.38.

5-(2,5-Dibromo-4-methylbenzyloxy)-1,3-benzenedimethanol (11b): A solution of $LiBH_4$ (0.3 g, 13.4 mmol) in THF (100 mL) was refluxed for 1 h, then cooled to room temperature, and a solution of **11a** (1.6 g, 3.39 mmol) in 50 mL THF was added dropwise. After addition the mixture was refluxed for further 6 h. The solvent was removed in vacuo, and the residue was acidified with diluted HCl. The resulting solid was separated by filtration, and recrystallized from toluene and methanol 1:1 (*v*/*v*) to give pure compound **11b** (1.24 g, 88%). ^{1}H NMR ([D$_6$]DMSO): $\delta = 7.73$ (s, 1H), 7.66 (s, 1H), 6.88 (s, 1H), 6.85 (s, 2H), 5.21 (t, 2H), 5.06 (s, 2H), 4.45 (d, 4H), 2.31 (s, 3H); ^{13}C NMR ([D$_6$]DMSO): $\delta = 157.97$, 144.12, 139.43, 135.68, 134.55, 132.90, 123.34, 121.48, 117.23, 110.84, 68.03, 62.81, 21.77.

2,5-Dibromo-4-methyl-1-[3,5-bis(bromomethyl)phenoxymethyl]benzene (2): A solution of PPh_3 (3.15 g, 12.02 mmol) in THF (15 mL) was added dropwise to a stirred solution of **11b** (2.0 g, 4.81 mmol) and CBr_4 (3.98 g, 12.02 mmol) in THF (10 mL) at 0 °C. Stirring was continued for another 1 h. Water was added and the aqueous layer extracted with CH_2Cl_2. After drying of the organic layer and removal of the solvent in vacuo the crude product was purified through a short column using CH_2Cl_2 as eluent, and recrystallized from CH_2Cl_2/hexane 1:5 (*v*/*v*) (2.2 g; 83%). ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.68$ (s, 1H), 7.44 (s, 1H), 7.06 (s, 1H), 6.93 (s, 2H), 5.03 (s, 2H), 4.44 (s, 4H), 2.36 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) 158.62, 139.81, 139.47, 134.86, 134.30, 132.39, 124.08, 122.57, 120.63, 115.51, 68.74, 32.67, 22.43; anal. calcd for $C_{16}H_{14}Br_4O$: C 35.46, H 2.60; found: C 35.24, H 2.58.

1-{3,5-Bis[dimethyl(1,1-dimethylethyl)silyloxy]phenoxymethyl}-4-methyl-2,5-dibromobenzene (15): For the first part see general procedure A: Compound **1** (4.9 g, 14.3 mmol), **14**·2H$_2$O (11.6 g, 71.4 mmol), K_2CO_3 (4.0 g, 29 mmol), and acetone (200 mL) were used. After reaction the solvent was evaporated to dryness, the residue was dispersed in water and filtrated. The solid was washed with water and dried in high vacuum. Crude **7** was obtained using silica gel chromatography eluting with CH_2Cl_2/diethyl ether 2:1 (*v*/*v*) gradually increasing to 1:1.

A mixture of crude **7** (2.67 g, 6.88 mmol), dimethyl(1,1-dimethylethyl)silylchloride (17.2 mL, 17.2 mmol), imidazole (1.36 g, 20.2 mmol), and DMF (30 mL) was stirred overnight at room temperature. After reaction, DMF was evaporated to dryness under high vacuum, the residue was dissolved in diethyl ether 20 mL and washed with water. The organic phase was dried over $MgSO_4$ and evaporated to dryness. The crude product was purified by silica gel column chromatography eluting with hexane gradually changing to CH_2Cl_2/hexane 1:7 to give pure **15** as a colorless solid (2.7 g, 64% from crude **7** or 31% from compound **1**). ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.64$ (s, 1H), 7.42 (s, 1H), 6.15 (d, 2H), 6.00 (t, 1H), 1.79 (s, 2H), 2.35 (s, 3H), 0.96 (s, 18H), 0.18 (s, 12H); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 159.54$, 157.17, 139.05, 135.46, 134.14, 132.26, 124.05, 120.41, 105.67, 100.85, 68.55, 25.67, 22.37, 18.20, −4.42; anal. calcd for $C_{26}H_{40}Br_2O_3Si_2$ (616.6): C 50.65 H 6.54; found: C 50.42 H 6.38.

General procedure for Suzuki polycondensation (SPC): A mixture of fourth generation macromonomer, 1,4-benzenediboronic acid propanediol ester (**16**), $NaHCO_3$, H_2O, and THF was carefully degassed before [Pd{P(*p*-tolyl)$_3$}$_3$] was added. The mixture was refluxed for 3 or 7 d under stirring. CH_2Cl_2 (200 mL) was added, the organic layer separated, and dried over $MgSO_4$. After removal of the solvent, the polymer was dissolved in CH_2Cl_2 (10 mL) and the obtained solution dropped into diethyl ether (300 mL). The precipitate was recovered by centrifugation, taken up in benzene, and freeze-dried.

Some specific comments regarding charging the reaction flask, a Schlenk tube with Rotaflo cock, with the components: The catalyst precursor was pre-weighed in a high quality glovebox ($H_2O < 1.5$ ppm, $O_2 < 1.2$ ppm) into an air-tight, light glass vessel. After removal from the glovebox this vessel was weighed precisely and the content poured into the Schlenk tube under a stream of nitrogen. Adhering material was left inside the vessel. The (almost) empty vessel was then re-weighed to get the accurate amount of catalyst precursor added. One single batch of catalyst precursor was used for as many entries as possible (for example: entries 6–9 and 12–16). The boronic acid ester **16** was used in crystalline form and weighed on precision scales using weighing paper from which it could be quantitatively transferred into the Schlenk tube (re-weighing).

Poly{2-[3,5-bis[3,5-bis[3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyloxy]-benzyloxy] benzyloxymethyl]phenoxymethyl-5-methyl]biphen-4,4′-diyl} (17): See general procedure for SPC. **4** (787 mg, 0.221 mmol), **16** (55.6 mg, 0.226 mmol), $NaHCO_3$ (0.49 g), H_2O (3 mL), THF (10 mL), and [Pd(PPh$_3$)$_4$] (2.8 mg, 1.1 mol-%) were used. The mixture was refluxed under N_2 for 3 d and purified by chromatography (740 mg, 96%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.22$ (broad, 86H), 6.95 (broad, 1H), 6.78 (broad, 2H), 6.53 (broad, 28H), 6.42 (broad, 14H), 4.87–4.68 (broad, 58H), 4.34 (broad, 8H), 2.23 (broad, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 159.94$, 159.84, 140.66, 139.88, 139.11, 136.64, 131.18, 128.44, 127.86, 127.47, 113.14, 106.23, 101.38, 72.01, 69.80, 20.29; anal. calcd for $[C_{232}H_{200}O_{31}]_n$ $(3484.1)_n$: C 79.98 H 5.78; found: C 78.95 H 5.83.

Poly {2-{3,5-bis{4-{1,1-bis{4,4′-bis{3,5-bis[3,5-bis(benzyloxy)benzyloxy]-benzyloxy}phenyl}ethyl}phenoxymethyl}phenoxymethyl}5-methyl]biphen-4,4′-diyl} (18): See general procedure for SPC. Compound **6** (577.8 mg, 0.148 mmol), **16** (36.6 mg, 0.149 mmol), $NaHCO_3$ (0.50 g), THF (20.0 mL), H_2O (10.0 mL), and [Pd{P(*p*-tolyl)$_3$}$_3$] (2.46 mg, 1.6 mol-%) were used. The mixture was refluxed for 7 d under N_2 and purified by chromatography (530 mg, 94%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.20$ (broad, 86H), 6.88 (broad, 15H), 6.71 (broad, 12H), 6.68–6.48 (broad, 36H), 4.83–4.72 (broad, 62H), 2.25 (broad, 3H), 1.93 (broad, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) 160.00, 159.89, 156.64, 141.94, 139.45, 139.11, 136.64, 130.17, 129.57, 129.13, 128.48, 127.90, 127.49, 126.86, 113.86, 106.89, 106.26, 105.61, 101.40, 100.77, 70.98, 69.87, 68.74, 50.51, 30.63; anal. calcd for $[C_{258}H_{220}O_{31}]_n$ $(3816.6)_n$: C 81.19 H 5.81; found: C 80.52 H 5.71.

Poly{2-[3,5-bis[3,5-bis[3,5-bis[3,5-bis(benzyloxy)benzyloxy] benzyloxy]-benzyloxy] benzyloxy]phenoxymethyl]-5-methyl]biphen-4,4′-diyl} (19): See general procedure for SPC. Compound **9** (781.5 mg, 0.221 mmol), **16** (54.6 mg, 0.222 mmol), $NaHCO_3$ (1.0 g), H_2O (9.0 mL), THF (20.0 mL), and [Pd{P(*p*-tolyl)$_3$}$_3$] (1.6 mg, 0.71 mol-%) were used. The mixture was refluxed for 7 d under N_2 and purified by chromatography (710 mg, 93%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.15$ (broad, 86H), 6.51 (broad, 28H), 6.48 (broad, 14H), 6.08 (broad, 3H), 4.78–4.68 (broad, 62H), 2.20 (broad, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 159.92, 139.10, 136.64, 129.07, 128.42, 127.83, 127.45, 126.83, 106.84, 106.21, 105.59, 101.99, 101.37, 70.90, 69.77, 68.64; anal. calcd for $[C_{230}H_{196}O_{31}]_n$ $(3484.1)_n$: C 79.93 H 5.72; found: C 79.51 H 5.61.

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