Dendronized Polymers: Increasing of Dendron Generation by the Attach-to Approach

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ABSTRACT: Dendronization with the first generation (G1) building block **10b** of the polystyrenes **13c** and **14c** carrying first (G1) and second generation (G2), amino-terminated appendant dendrons is reported. Comparison of the ^{1}H and ^{13}C NMR spectra of the resulting G2 and G3 polystyrenes (**15**, **17a**) with those recorded of the same polymers independently prepared from the corresponding G2 and G3 macromonomers **16** and **12**, respectively, proved the degree of coverage to be virtually 100%. This is the first example of a convergent synthesis of a G3 polymer, which will considerably widen the synthetic access into this class of macromolecules.

Introduction

There are beautiful applications of the convergent growth concept for dendrimer synthesis. High generation products were obtained with comparably low effort, yet with a remarkably high degree of structural perfection.[1] Dendronized polymers, which may also be called polymers with appendant dendrons or dendrimers with a polymeric core, form a class of macromolecules which is presently being given considerable attention.[2] One reason for this is the stiffening of the polymers' backbone by the dendritic substituents. This rather unique feature allows, i.e., individualization of single macromolecules and their manipulation on solid surfaces.[2c−e] Some of these polymers, specifically those with a highly dense dendritic layer, can be considered nanoscale cylindrical objects.[3]

Up to now, dendronized polymers were synthesized either by the attach-to strategy in which dendrons of the final size were attached to the anchor groups of mostly poly(*p*-phenylene)-type backbones or, alternatively, by polymerizing macromonomers which already contain the dendron of final size. The first route met only with limited success. Complete coverage has not been achieved yet beyond second generation (G2) dendrons.[4] The second route proved more successful. A variety of both chain-growth and step-growth macromonomers with G2[2a,f] and G3 dendrons[5] and even one with a G4 appendant dendron[6] were polymerized to high molar mass polymers.

In this contribution the convergent (attach-to) growth concept was applied to dendronized polymers to see whether their dendrons' generation can be increased by this mixed strategy. An especially important target was the synthesis of G3 dendronized vinyl polymers, which are otherwise difficult to prepare. First the synthesis of the new amino-terminated G1 and G2 dendronized polystyrenes **13** and **14,** which serve as starting materials for the dendronization, will be described, and then the chemical modification of these polymers with the G1 building block **10b** carrying an activated ester function at focal point to give the corresponding G2 and G3 polystyrenes **15** and **17a**, respectively, will be reported. Finally, the structures of these polymers will be proven by independent synthesis starting from the corresponding dendritic macromonomers.

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Results and Discussion

Monomer and Polymer Synthesis. The synthetic sequences to the dendritic macromonomers **7**, **9**, and **12** are displayed in Schemes 1−3. The general features are as follows.

(a) All macromonomers carry triphenylmethyl (trityl) or trimethylsilylethoxycarbonyl (teoc) protected amine functions in the periphery (**7**, 2; **9**, 4; **12**, 8). The amines were selected because, considering their rich chemistry, they are ideal functional groups to bring about various chemical modifications of the targeted polymers including dendronization and biorelated modifications. This matter also relates to one of our major goals in this research, which is to learn how to do surface engineering of dendritic nanocylinders.

Trityl and teoc were chosen as protecting groups for cost and solubility reasons, respectively. The more commonly used *tert*-butyloxycarbonyl (boc) as protecting group for amines was also tried but found to be much inferior mostly for purification reasons. The precursor for trityl is commercially available at low cost, the solubility of tritylated compounds, however, is generally not very high. Since a high solubility of macromonomers can be critical in achieving high molar mass polymer,[7] teoc was also tried despite its relatively high cost and the additional synthetic effort associated with its use.

(b) The construction principle of monomers **7** and **9** rests upon branching unit **3** with two bromines and an allylic function. This substitution pattern makes it ideally suited for a convergent synthesis of aryl/alkyl hydrocarbon based dendrons by repeated application of the two steps hydroboration with 9-BBN and alkyl/aryl Suzuki cross-coupling (SCC).[8] Moreover, the polymerizable unit (here, styrene) can be introduced by the same chemistry.

(c) Monomers **7** and **9** are hydrocarbons and, thus, unpolar (except for the peripherial functional groups). They have 1,3,5-substituted benzenes as branching units and trimethylenes as branches. Macromonomer

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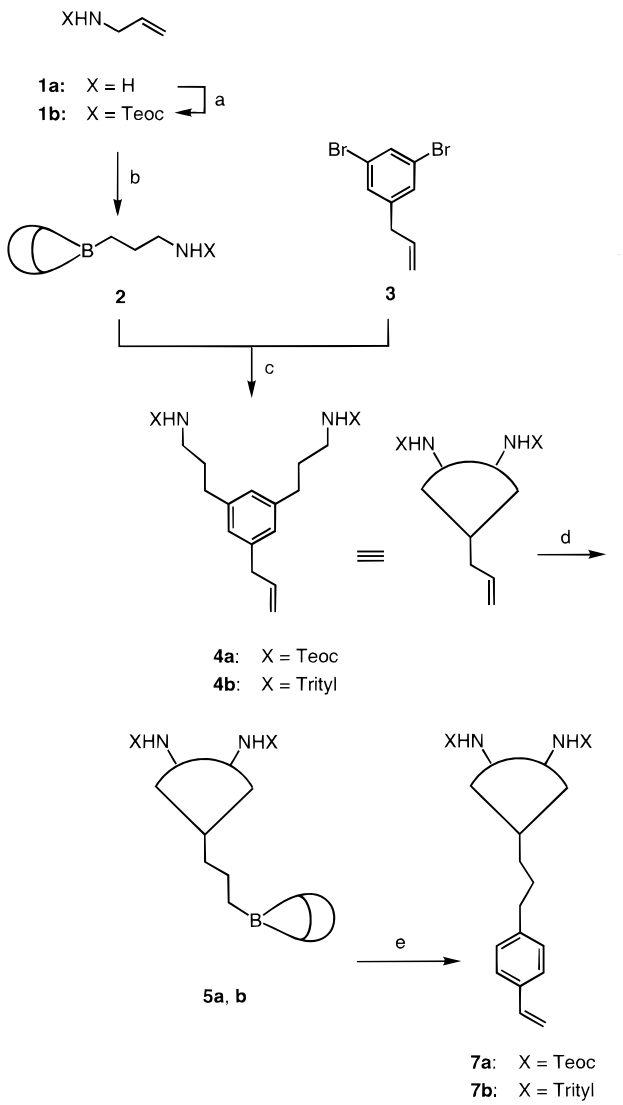
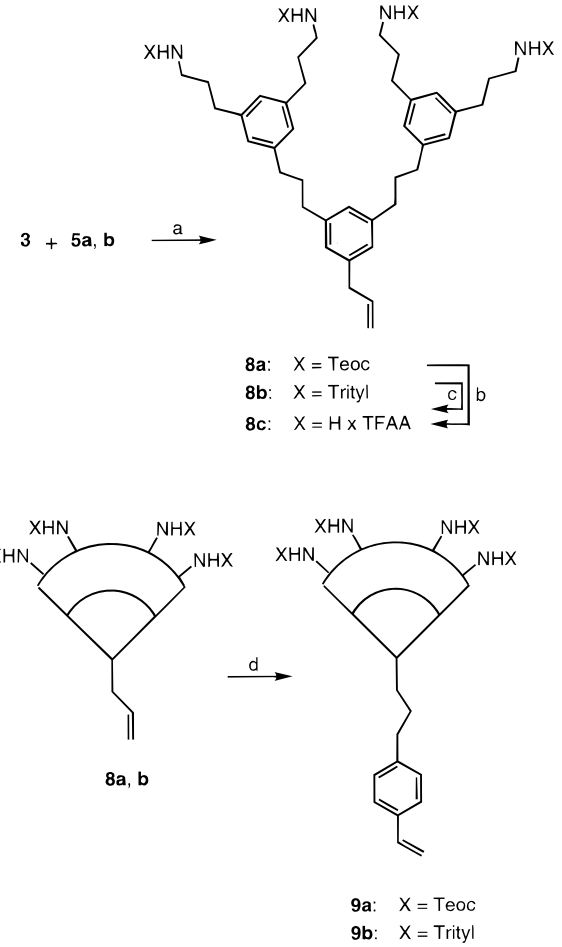
Scheme 1. Reagents and Conditions: (a) Trimethylsilyl Ethyl Chloroformate, 1a, KOH, THF/H_2O, RT, 24 H, (58%); (b) 1b, 9-BBN, THF, RT, 24 H, (96%); (c) 2, 3, 3 M NaOH, $Pd(PPh_3)_4$, 77 °C, 48 H, (79%) for 4a; (d) 4a (4b), 9-BBN, THF, RT, 24 h; (e) 5a (4b), 6, 1 M NaOH, $Pd(PPh_3)_4$, 77 °C , 40 H, (67%) for 7a, (69%) for 7b



Scheme 2. Reagents and Conditions: (a) 3, 5a (5b), THF, 3 M NaOH, $Pd(PPh_3)_4$, 77 °C, 48 h (70%) for 8a, (61%) for 8b; (b) Trifluoroacetic Acid, RT, 24 h; (c) Trifluoroacetic Acid, Methanol, RT, 48 h; (d) 1. 8a (8b), 9-BBN, THF, RT, 24 h. 2. 1 M NaOH, $Pd(PPh_3)_4$, 77 °C, 48 H, (45%) for 9a, (30%) for 9b



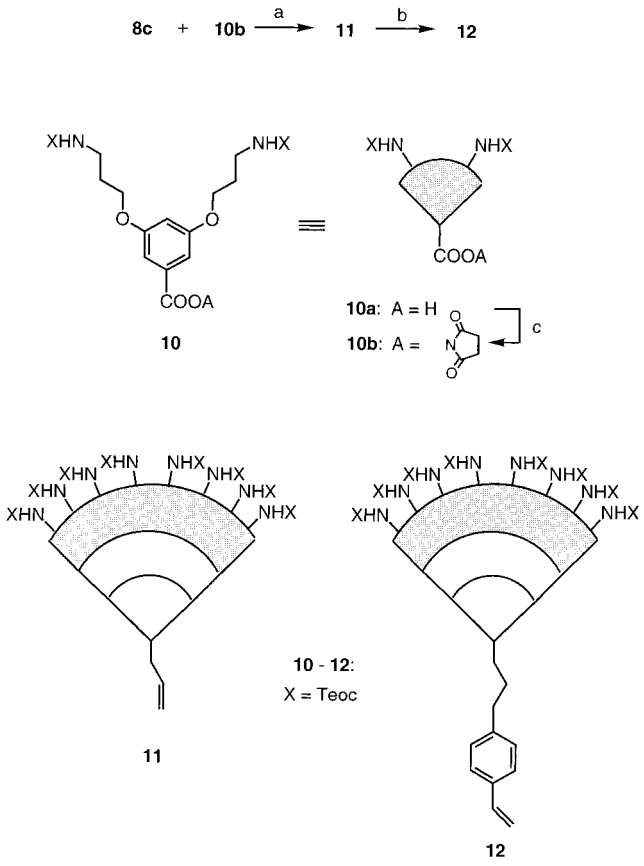
12 differs from **9** in that it has two unpolar generations going from its polymerizable unit to the periphery which are followed by a more polar terminal one whose polarity rests basically upon the four amide bonds. As for **7** and **9**, the peripherial amine groups of **12** provide the option for further increased polarity at a later stage, i.e., by quaternization.

The individual synthetic steps are straightforward and not commented further here. The macromonomers were prepared on the gram scale (**7a**, 3 g; **7b**, 4 g; **9a**, 1 g; **9b**, 1 g; **12**, 0.5 g). Purification was done by column chromatography. Characterization rests upon the ^1H and ^{13}C NMR spectra including full signal assignments, mass spectra, and correct[9] data from combustion analyses.

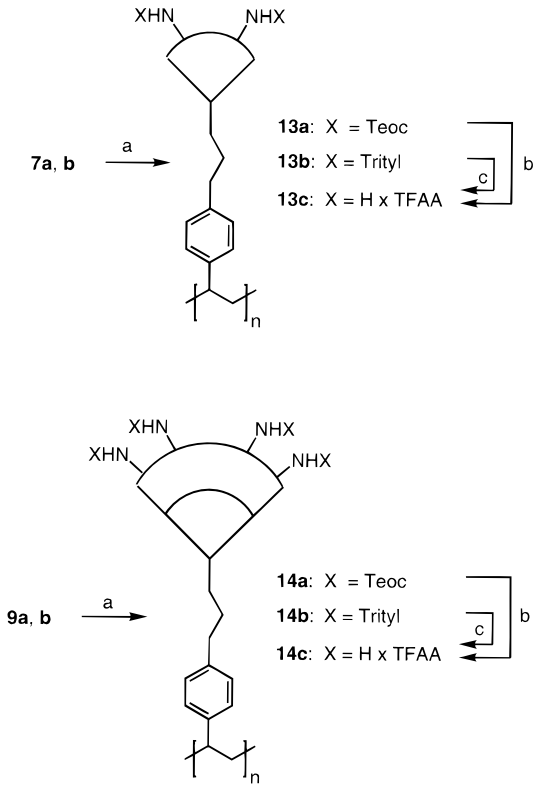
Macromonomers normally give high molar mass products only in a narrow and high concentration range.[7,10] The radically initiated polymerizations of monomers **7**, **9**, and **12** were therefore done in highly concentrated solutions (Schemes 4 and 5). The results are summarized in Table 1. Except for entry 2 the concentrations were not systematically varied but chosen after three to four orienting experiments. In the case of monomer **7b** (entry 2), however, they were varied broadly (see Experimental Section), and the best result is stated in Table 1. The molar masses were obtained by GPC vs polystyrene standard and therefore have to be considered with care. GPC grossly underestimates molar masses of dendronized polymers because it does not take into account their much higher molar mass per unit length than in the parent polystyrene. Factors, by which GPC underestimates the actual molar masses, may range between 1.5 and 4.[11]

The following conclusions can be drawn from these data. Best results regarding yields and molar masses are obtained for the teoc protected monomers. Tritylated monomers are clearly inferior (compare entries 1/2 and 4/5). Changing the solvent from toluene to diethyl ketone improves the situation for polymer **13b** obtained from tritylated **7b** but the molar masses achievable for polymer **14a** by using **7a** still cannot be reached (compare entries 2/4). A reason for the superiority of teoc over trityl monomers may be the higher solubility of the former which allows one to apply higher concentrations. It should be noted here that the polymerization mixtures of tritylated monomers in Table 1 (entries 2, 3, and 5) were not homogeneous. The actual concentrations are therefore lower than the numbers stated. All

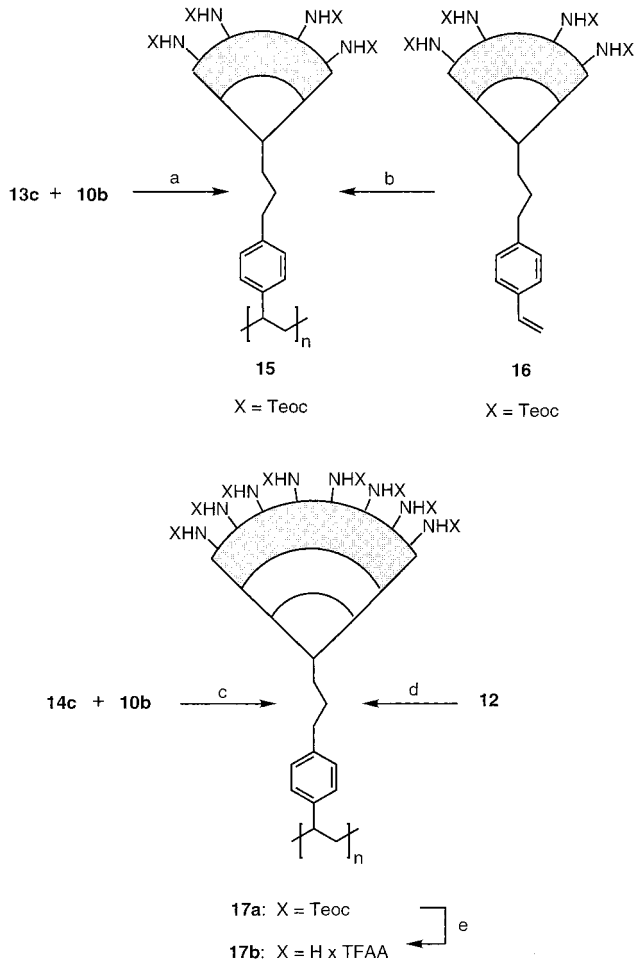
Scheme 3. Reagents and Conditions: (a) 8c, 10b, Triethylamine, Methanol, 24 H, RT, (57%); (b) (1) 11, 9-BBN, THF, RT, 24 h, (2) *p*-Bromostyrene (6), 1 M NaOH, $Pd(PPh_3)_4$, 77 °C, 40 H, (40%); (c) 10b, *N*-Hydroxysuccinimide, DCC, CH_2Cl_2, 24 H, RT, (89%)



Scheme 4. Reagents and Conditions: (a) See Table 1; (b) Trifluoroacetic Acid, RT, 24 h; (c) Trifluoroacetic Acid, Methanol, RT, 48 h



Scheme 5. Reagents and Conditions: (a) 13c, 10b, Triethyl Amine, Methanol/CH_2Cl_2, RT, 48 h; (b) 16, 3 mol % ^{t}BPB, Toluene, 90 °C, 48 h; (c) 14c, 10b, Triethyl Amine, Methanol/ CH_2Cl_2, RT, 48 h; (d) See Table 1; (e) Trifluoroacetic Acid, RT, 24 h



polymers were fully characterized including completely assigned high-field NMR-spectra and correct data from combustion analysis.

Deprotection and Dendronization of G1 and G2 Dendronized Polystyrenes 13 and 14. Samples of all polymers with the molar masses given in Table 1 were deprotected with trifluoroacetic acid either in methanol solution (trityl protected polymers) or neat (teoc protected polymers).[12] The acid was used in an excess of 1−2 equiv per functional group. Whereas for the teoc polymers a single acid treatment was sufficient to drive deprotection to completion, it had to be repeated 2−3 times for the trityl polymers. The completeness of the deprotection was proven by highly resolved ^{1}H NMR spectra with an excellent signal-to-noise ratio. The signals of the teoc group at $\delta = -0.05$, 0.90, and 4.10 ppm and that of the trityl group at $\delta = 7.10$ and 7.38 disappeared completely. These spectra are not shown here because similar ones have already been published.[11] The resulting polymers **13c** and **14c** are fully soluble in methanol and water. To bring about the dendronization, the methanolic solutions containing triethylamine to deprotonate the ammonium functions were treated at room temperature with a 2-fold excess per ammonium function of the dendritic building block **10b**, which has an activated ester at its focal point (Scheme 5). The decreasing solubility of the polymers in methanol in the course of the dendronization caused

Table 1. Polymerization of G1 and G2 Macromonomers and The Results

entry	polymer	monomer concn (mol/L)	initiator[a]	T (°C)	solvent	M_n ($\times 10^4$)[b]	M_w/M_n	yield (%)[c]	P_n
1	**13a**	0.68	AIBN[d]	55	toluene	3.8	2.44	85	60
2	**13b**	0.62	^{t}BPB[e]	90	toluene	2.1	1.84	17	25
3	**13b**	0.62	^{t}BPB	90	diethyl ketone	2.6	2.78	79	32
4	**14a**	0.45	^{t}BPB	90	toluene	5.0	1.94	86	39
5	**14b**	0.45	^{t}BPB	90	diethyl ketone	2.0	1.76	28	14
6	**17a**	0.26	^{t}BPB	90	toluene	3.7	1.35	63	13

[a] 3 mol %. [b] Determined from raw material by GPC with THF as the eluent and polystyrene standard. [c] Determined by ^{1}H NMR spectroscopy of the raw product. [d] 2,2′-Azobis(isobutyronitrile). [e] *tert*-Butyloxybenzoate.

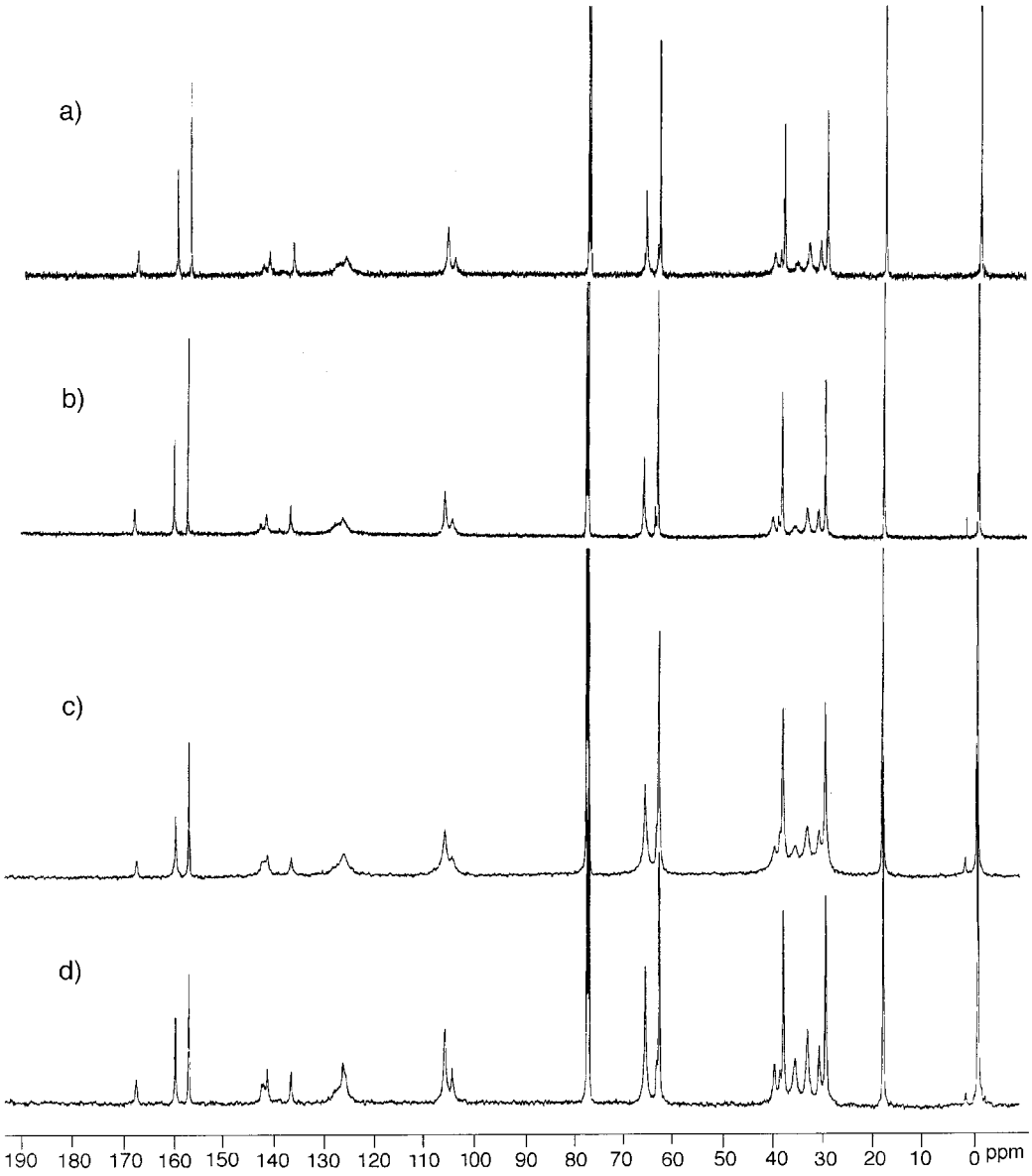


Figure 1. ^{13}C NMR spectra of polymers *at*-**15**, *mm*-**15**, *at*-**17a**, and *mm*-**17a** (a−d) in $CDCl_3$ at 20 °C.

by their decreasing polarity was accounted for by the addition of methylene chloride after a few hours of reaction (MeOH:CH_2Cl_2 = 1:1). After removal of the solvents and the base in a vacuum, the remaining materials, with the proposed structures **15** and **17a**, respectively, were precipitated into methanol/water (4:1) whereby the accompanying salts dissolved. This process had to be repeated several times in order to completely remove excess **10b** or its derivatives. The losses of polymer associated with this somewhat tedious procedure fortunately remained below some 20−25%.

To determine the degree of dendronization, polymers **15** and **17a** were investigated by high-field ^{1}H and ^{13}C NMR spectroscopy. All signals appeared at the expected shifts and with the ^{1}H integration ratios required for a complete coverage. Because of the considerable widths at half-height of the signals involved and the maximally achievable yet relatively low concentration,[13] the accuracy of NMR integration was considered insufficient to prove this important point. Therefore, polymers **15** and **17a** were prepared independently from their corresponding macromonomers **16** and **12**, respectively.

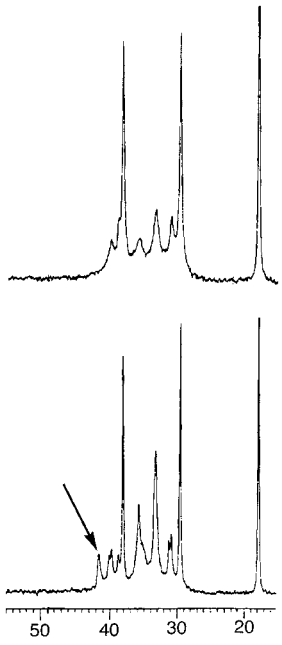


Figure 2. Parts of ^{13}C NMR spectra of *at*-**17a** with a proposed complete (top) and a 70% G1 dendron coverage (bottom). The signal of the α-methylene carbon of nondendronized amines can be identified at $\delta = 42$ ppm (bottom).

They carry the same G2 and G3 dendrons as in **15** and **17a**. To differentiate between the polymers of proposedly the same structure but different synthetic origin, the prefixes *at* for attach to and *mm* for macromonomer are used in the following. The ^{1}H NMR spectra of *at*-**15** and *mm*-**15** as well as the ones of *at*-**17a** and *mm*-**17a** are virtually superimposable (not shown). Figure 1 shows the ^{13}C NMR spectra of *at*-**15**, *mm*-**15**, *at*-**17a**, and *mm*-**17a** (parts a−d). As can be seen, these spectra are also pairwise virtually superimposable except for the fact that the line shapes of the latter two differ somewhat presumably due to a resolution problem. Most importantly, there is no indication of unreacted amine functionality in these spectra. Amino-functionalized methylene carbons typically absorb at $\delta = 42$ ppm.[14] This shift is so close to the signals absorbing in the range $\delta = 29-40$ that a confirmation seemed necessary that free amines can be unambiguously detected. Polymer **14c** was therefore reacted with less than stoichiometric amounts of **10b** (0.70 equiv per amine function) in order to deliberately create free, nondendronized amines. According to the TLC and GPC of the raw material, all of the **10b** could be brought to reaction, and it is therefore reasonable to assume that the resulting *at*-**17a** contains roughly 30% of the unreacted amines. Figure 2 compares parts of the ^{13}C NMR spectrum of this uncompletely covered *at*-**17a** (bottom) with one which has the maximum achievable coverage (top spectrum). The bottom spectrum shows clearly a signal well-separated off at $\delta = 42$ where nothing is to be seen in the top spectrum.

Besides this spectral evidence, the completeness of the coverage is also indicated by combustion analysis. The data obtained are in excellent agreement with the calculated ones not only for *mm*-**15** and *mm*-**17a** but also for *at*-**15** and *at*-**17a**. The calculated values are quite sensitive to structural imperfections. Assuming that 5%, 10%, or 15% of the amine anchor groups of *at*-**17a** did not react with **10b**, the value for carbon increases from 62.12 for the structurally perfect material to 62.39, 62.67, and 62.97, respectively. The observed values for carbon from two independent determinations are 61.94 and 61.71.

Though each of the points mentioned has its individual weaknesses, together they provide convincing evidence for the proposed complete coverage of polymers **13c** and **14c** with the G1 dendritic building block **10b**. Interestingly the GPC molecular weights decrease through the dendronization. For example, a sample of polymer **14a** with $P_n = 40$, $M_n = 50\,000$ gave *at*-**17a** with $M_n = 37\,000$ and a yield of 76%. This underlines the difficulty to use polystyrene as standard for dendronized polymers.

In sum, this work has shown that the convergent growth concept can be applied to dendronized polymers. For the first time a G3 dendronized vinyl polymer (**17a**) has been prepared not (only) via the macromonomer route but also by attaching a G1 dendron to the G2 precursor polymer **14c**. **17a** is the second reported case for a vinyl polymer with G3 dendrons and compound **12** for a G3 vinyl macromonomer to actually polymerize. Polymers **13, 14**, and **17a** have an unpolar interior which is surrounded by the polar protected functional groups (**13**, **14**) and a "layer" of polar amide functions between generations 2 and 3 (**17a**), respectively. This structural characteristic may be used to build ordered layers with a regular array of unpolar channnels surrounded by a polar matrix. The deprotected polymers **13c**, **14c**, and **17b** constitute a new class of polyelectrolytes with an unusually high number of charges per repeat unit. The experiments described in this paper may also be viewed as key prerequisites for surface engineering of dendritic, cylindrically shaped nanoobjects.

Experimental Section

Compounds **1a**, 9-BBN, *p*-bromostyrene (**6**), and trifluoroacetic acid were purchased from Aldrich. Compounds **3**,[7b] **4b**,[7b] **10a**,[10] and **16**[7b] were prepared according to literature procedures. All solvents were dried under standard conditions. ^{1}H and ^{13}C NMR spectra: Bruker AM 270 and AC 500 spectrometer. MS: Varian MAT 711 spectrometer. Elemental analysis: Perkin-Elmer EA 240. Gel permeation chromatography (GPC): Waters ultra-Styragel linear column (polystyrene standards, THF eluent, room temperature, UV detection 254 nm).

3-[2-(Trimethylsilyl)ethoxycarbonylamino]propene (1b). To a solution of 24 g (203 mmol) of 2-trimethylsilylethanol and 56 g (406 mmol) of anhydrous potassium carbonate in 200 mL of toluene was added 130 mL of a 20% solution of phosgene (225 mmol) in toluene and stirred for 1 h at 0 °C. After the ice bath was removed, the solution was stirred for another h. The solvent was removed in a vacuum at a bath temperature less than 40 °C in a well-ventilated hood. A mixture of the raw oil, 6.84 g (120 mmol) of allylamine disolved in 150 mL of THF, and 8.5 g (152 mmol) of potassium hydroxide disolved in 85 mL of water was stirred at 20 °C for 24. The organic layer was separated and washed with water (35 100 mL) and dried with magnesium sulfate. Distillation (65 °C, 10^{-2} mbar) gave 14.0 g of **1b** (58%) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ − 0.04 (s, 9 H, TMS), 0.94 (t, 2 H, TMSCH_2), 3.72 (t, 2 H, NHCH_2), 4.13 (t, 2 H, OCH_2), 4.70 (br, 1 H, NH), 5.10 (m, 2 H, CH_2=CH), 5.74 (m, 1 H, CH_2=CH). ^{13}C NMR ($CDCl_3$): δ −1.5 (TMS), 17.7 (TMSCH_2), 43.3 (NHCH_2), 63.0 (OCH_2), 115.8 (CH=CH_2), 134.7 (CH=CH_2), 156.6 (NHCOO). MS (80 ev), *m*/*z* (%): 201.0 (1.1) [M^+]. Anal. Calcd for $C_9H_{19}SiO_2N$ (201.3): C, 53.69; H, 9.51; N, 6.96. Found: C, 52.42; H, 9.20; N, 6.60. HRMS: calculated, 201.11851; found, 201.11633; deviation, 2.2 (mmu).

***B*-[2-(Trimethylsilyl)ethoxycarbonylamino]propyl-9-BBN (2).** To a dry 250 mL Schlenck flask was added 7.5 g of

1b (37.5 mmol), 5.0 g (41.2 mmol) of 9-BBN and 80 mL of dry THF. The mixture was stirred under nitrogen for 24 h. Compound **2** in THF was used without further purification. The conversion was determined to be 96% (NMR).

Allyl-3,5-bis[3-[2-(trimethysilyl)ethoxycarbonylamino]-propyl] benzene (4a). To a solution of compound **2** (36 mmol) in 100 mL of THF, was added 18 mL of aqueous 3 M NaOH, 0.63 g (0.55 mmol) of tetrakis(triphenylphosphine)palladium-(0), and 4.0 g (14.4 mmol) of allyl-3,5-dibromobenzene. The mixture was stirred for 48 h at 77 °C. The organic layer was separated, washed with brine, and dried ($MgSO_4$). Chromatographic separation (silica gel, hexane/ethyl acetate (4:1/v:v) yielded 6.0 g (79%) of **4a** as colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.00 (s, 18 H, TMS), 0.95 (t, 4 H, TMSCH_2), 1.77 (m, 4 H, $CH_2CH_2CH_2$), 2.55 (t, 4 H, $ArCH_2$), 3.18 (m, 4 H, NHCH_2), 3.30 (d, 2 H, $ArCH_2CH$), 4.14 (t, 4 H, OCH_2), 4.70 (br, 2 H, NH), 5.06 (m, 2 H, CH_2=CH), 5.92 (m, 1 H, CH_2=CH), 6.81 (s, 3 H, ArH). ^{13}C NMR ($CDCl_3$): δ −1.5 (TMS), 17.7 (TMSCH_2), 31.6 (CH_2), 32.8, 40.0, 40.4, 62.8 (OCH_2), 115.7, 126.2, 126.3, 137.4, 140.2, 141.6 (Ar), 156.7 (NHCOO). MS (80 ev), *m*/*z* (%): 520.2 (8.73) [M^+]. Anal. Calcd for $C_{27}H_{48}N_2O_4Si_2$ (520.8): C, 62.26; H, 9.29; N, 5.38. Found: C, 61.62; H, 9.01; N, 5.15.

***B*-{3,5-Bis[3-[2-(trimethysilyl)ethoxycarbonylamino]-propyl]benzylpropyl}-9-BBN (5a). 5a** was prepared by the method for compound **2**, using 1.08 g (8.8 mmol) of 9-BBN and 3.8 g (7.4 mmol) of **4a** in 20 mL of THF. The solution was used without further treatment.

***B*-{3,5-Bis[3-triphenylmethylaminopropyl]benzyl-propyl}-9-BBN (5b). 5b** was prepared by the method for compound **2**, using 5.4 g (7.5 mmol) of **4b**, 1.1 g (9.0 mmol) of 9-BBN, and 50 mL of dry THF. The resulting compound **5b** was used without purification.

4-Vinyl{3,5-bis[3-[2-(trimethylsilyl)ethoxycarbonyl-amino]propyl]benzyl}propylbenzene (7a). To a solution of **5a** (7.4 mmol) in THF were added 20 mL of aqueous 1 M NaOH, 0.2 g (0.18 mmol) of tetrakis(triphenylphosphine)-palladium(0), and 1.9 g (10.4 mmol) of 4-bromostyrene. The mixture was stirred for 40 h at 77 °C. The organic layer was separated, washed with brine, and dried ($MgSO_4$). Chromatographic separation (silica gel, hexane/ethyl acetate (3.5:1/v:v) gave 3.0 g (67%) of **7a** as colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.03 (s, 18 H, TMS), 0.95 (t, 4 H, TMSCH_2), 1.77 (m, 4 H, $CH_2CH_2CH_2$), 1.90 (m, 2 H, $CH_2CH_2CH_2$), 2.57 (t, 6 H, $ArCH_2$), 2.61 (t, 2 H, $ArCH_2$), 3.15 (m, 4 H, NHCH_2), 4.14 (t, 4 H, OCH_2), 4.75 (br, 2 H, NH), 5.19 (d, 1 H, CH=CH_2), 5.70 (d, 1 H, CH=CH_2), 6.69 (dd, 1 H, CH_2=CH), 6.81 (s, 3H, ArH), 7.23 (AA′BB′, 4 H, ArH). ^{13}C NMR ($CDCl_3$, 125 MHz): δ −1.5 (TMS), 17.7 (TMSCH_2), 31.6, 32.8, 32.9, 35.2, 40.4 (CH_2), 62.8 (OCH_2), 112.8, 126.1, 126.2, 128.5, 135.1, 136.6, 141.5, 142.0, 142.4 (Ar), 156.7 (NHCOO). MS (80 ev), *m*/*z* (%): 624.0 (3.26) [M − H]$^+$. Anal. Calcd for $C_{35}H_{56}N_2O_4Si_2$ (625.0): C, 67.26; H, 9.03; N, 4.48. Found: C, 66.59; H, 8.79; N, 4.27.

4-Vinyl{3,5-bis[3-triphenylmethylaminopropyl]benzyl}-propylbenzene (7b). Compound **7b** was prepared according to the same procedure as for **7a**, using **5b** (7.5 mmol) in 50 mL of THF, 16 mL of 1 M NaOH, and 2.1 g (11 mmol) of *p*-bromostyrene. Chromatographic separation [silica gel, hexane/THF (30:1/v:v)] furnished 4.2 g (69%) of **7b** as a viscous oil. ^{1}H NMR ($CDCl_3$): δ 1.60 (s, 2 H, NH), 1.82 (q, 4 H, CH_2CH_2-CH_2), 1.96 (q, 2 H, $ArCH_2CH_2$), 2.27 (t, 4 H, $NHCH_2$), 2.65 (m, 8 H, $ArCH_2$), 5.26 (d, 1 H, CH=CH_2), 5.75 (d, 1 H, CH=CH_2), 6.74 (dd, 1 H, CH = CH_2), 6.83 (s, 3 H, ArH), 7.15−7.60 (m, 34 H, ArH). ^{13}C NMR ($CDCl_3$): δ 32.6, 32.9, 33.7, 35.3, 43.4, 70.8, 112.8, 125.8, 126.1, 127.7, 128.6, 136.6, 142.1, 142.3, 146.2. MS (EI, 80 ev), *m*/*z* (%) 820.1 (1,64) [M^+]. Anal. Calcd for $C_{61}H_{60}N_2$ (820.1): C, 89.27; H,7.32; N, 3.41. Found: C, 87.93; H, 7.32; N, 3.04.

Allyl-3,5-bis{3-{3,5-bis[3-[2-(trimethylsilyl)ethoxy-carbonylamino]propyl]benzyl}propyl}benzene (8a). Compound **8a** was obtained according to the same procedure as for **4a**. To a solution of compound **5a** (7.4 mmol) in 20 mL THF were added 4 mL of aqueous 3 M NaOH, 0.14 g (0.12 mmol) of tetrakis(triphenylphosphine)palladium(0), and 0.94 g (3.4 mmol) of **3**. The mixture was stirred for 48 h at 77 °C. After workup, chromatographic separation [silica gel, hexane/ethyl acetate (3:2/v:v)] yielded 2.8 g of **8a** (70%). ^{1}H NMR ($CDCl_3$, 270 MHz): δ 0.00 (s, 36 H, TMS), 0.97 (t, 8 H, TMSCH_2), 1.78 (m, 8 H, $NHCH_2CH_2CH_2$), 1.88 (m, 4 H, $ArCH_2CH_2CH_2Ar$), 2.54 (t, 16 H, $ArCH_2$), 3.18 (m, 8 H, NHCH_2), 3.30 (d, 2 H, $ArCH_2CH$), 4.12 (t, 8 H, OCH_2), 4.74 (br, 4 H, NH), 5.06 (m, 2 H, CH_2=CH), 5.93 (m, 1 H, CH_2=CH), 6.80 (s, 9 H, ArH). ^{13}C NMR ($CDCl_3$, 62 MHz): δ −1.5 (TMS), 17.7 (TMSCH_2), 31.6 (CH_2), 32.8, 33.0, 35.5, 40.1, 40.5, 62.7 (OCH_2), 115.5, 125.1, 125.8, 126.1, 126.3, 137.6, 139.8, 141.4, 142.3, 142.5, 156.7 (NHCOO). MS (EI, 80 ev), *m*/*z* (%): 1158.8 (2.20) [M − H]$^+$. Anal. Calcd for $C_{63}H_{106}N_4O_8Si_4$ (1159.7): C, 65.24; H, 9.21; N, 4.83. Found: C, 64.38; H, 8.80; N, 4.60.

Allyl-3,5-bis{3-{3,5-bis[3-triphenylmethylaminopropyl]-benzylpropyl}benzylpropyl}benzene (8b). 8b was obtained by the method for **4a**, using 6.4 g (9.0 mmol) of **4b**, 1.32 g (10.8 mmol) of 9-BBN, and 28 mL of dry THF and subsequently, 1.0 g (3.6 mmol) of **3**, 20 mL of 1 M NaOH, and 0.08 g of $Pd(PPh_3)_4$. Chromatographic separation [silica gel, hexane/ethyl acetate (2:1/v:v)] gave 3.4 g (61%) of **8b**. ^{1}H NMR ($CDCl_3$): δ 1.55 (s, 4 H, NH), 1.87 (dt, 8 H, CH_2CH_2NH), 1.95 (dt, 4 H, $CH_2CH_2CH_2$), 2.25 (t, 8 H, CH_2NH), 2.60 (m, 16 H, $ArCH_2$), 3.41 (d, 2 H, CH_2CH=CH_2), 5.19 (m, 2 H, CH=CH_2), 6.03 (m, 1 H, CH=CH_2), 6.83 (s, 6 H, ArH), 6.90 (s, 3 H, ArH), 7.24 (m, 36 H, ArH), 7.48 (d, 24 H, ArH). ^{13}C NMR ($CDCl_3$): δ 32.5, 33.0, 33.7, 35.6, 40.2, 43.5, 70.8, 115.5, 125.7, 125.8, 126.1, 126.4, 127.7, 128.6, 137.7, 139.8, 142.3, 146.2. FAB; *m*/*z* (%): 1552.9 (3.9) [M^+]. Anal. Calcd for $C_{115}H_{114}N_4$ (1553.2): C, 89.03; H, 7.35; N, 3.61. Found: C, 88.13; H, 7.25; N, 3.76.

Allyl-3,5-bis{3-[3,5-bis(3-aminopropyl)benzyl]propyl}-benzene (CF_3CO_2H)$_4$ (8c). To a solution of 4.5 g (2.9 mmol) of **8b** in 8 mL of methanol and 8 mL of dichloromethane was added dropwise 5 mL of trifluoroacetic acid with stirring at 0 °C. Then, the solution was stirred for 24 h at room temperature. After removal of the solvents, 10 mL of diethyl ether and 5 mL of water was added. The aqueous layer was separated and the extraction was repeated for 3 times. The combined aqueous layer were dried after removal of water in a vacuum to give 2.3 g (76%) of **8c** as white solid. ^{1}H NMR (CD_3OD): δ 1.95 (m, 12 H, $CH_2CH_2CH_2$), 2.65 (m, 16 H, CH_2Ar), 2.92 (t, 8 H, C$H_2NH_3^+$), 3.32 (d, 2 H, CH_2CH=CH_2), 5.05 (m, 2 H, CH=CH_2), 5.93 (m, 1 H, CH=CH_2), 6.92 (s, 3 H, ArH), 6.94(s, 6 H, ArH). ^{13}C NMR (CD_3OD): δ 30.2, 33.4, 34.6, 36.4, 36.5, 40.3, 41.1, 115.7, 118.2 (q, CF_3CO_2), 126.9, 127.3, 127.5, 139.1, 141.2, 143.6, 144.4, 161.7 (q, CF_3COO). FAB; *m*/*z* (%): 583 (27) [cluster of tetraamine] [M^+ − 3$5CF_3COOH$ − CF_3COO^-]. Anal. Calcd for $C_{47}H_{62}N_4O_8F_{12}$ (1038.0): C, 54.33; H, 6.01; N, 5.39. Found: C, 52.91; H, 5.83; N, 5.99.

4-Vinyl{3,5-bis{3-{3,5-bis[3-[2-(trimethylsilyl)ethoxy-carbonylamino]propyl] benzyl}propyl}benzylpropyl}-benzene (9a). G-2 monomer **9a** was prepared according to the same procedure as for **7a**, using 2.6 g of **8a** (2.2 mmol), 0.32 g of 9-BBN (2.6 mmol), 10 mL of dry THF. Subsequently, 6 mL of 1 M NaOH, 0.05 g of $Pd(PPh_3)_4$, and 0.6 g (3.3 mmol) of *p*-bromostyrene were added. Chromatographic separation [silica gel, hexane/ethyl acetate (1.7:1/v:v)] yielded 1.25 g (45%) of **9a**. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.00 (s, 36 H, TMS), 0.97 (t, 8 H, TMSCH_2), 1.78 (m, 8 H, $NHCH_2CH_2CH_2$), 1.88 (m, 6 H, $ArCH_2CH_2CH_2Ar$), 2.55 (m, 20 H, $ArCH_2$), 3.18 (m, 8 H, NHCH_2), 4.12 (t, 8 H, OCH_2), 4.74 (br, 4 H, NH), 5.18 (d, 1 H, CH=CH_2), 5.70 (d, 1 H, CH=CH_2), 6.69 (dd, 1 H, CH=CH_2), 6.80 (s, 9 H, ArH), 7.25 (AA′BB′, 4 H, ArH). ^{13}C NMR ($CDCl_3$): δ −1.5 (TMS), 17.7, 31.6, 32.9, 33.0, 35.2, 35.4, 40.5, 62.8, 112.8, 125.8, 126.0, 126.1, 128.2, 128.6, 136.6, 141.5, 142.0, 142.1, 142.6, 156.8. FAB; *m*/*z* (%): 1287.0 (9.27) [M^++Na]. Anal. Calcd for $C_{71}H_{114}N_4O_8Si_4$ (1264.0): C, 67.46; H, 9.09; N, 4.43. Found: C, 66.86; H, 8.84; N, 4.30.

4-Vinyl{3,5-bis{3-{3,5-bis[3-triphenylmethylamino-propyl]benzyl}propyl}benzylpropyl}benzene (9b). 9b was produced by the same method as for **7a**, using 3.2 g (2.0 mmol) of **8b**, 0.30 g (2.5 mmol) of 9-BBN, and 16 mL of dry THF. Subsequently, 6 mL of 1 M NaOH, 0.04 g of $Pd(PPh_3)_4$, and 0.51 g (2.8 mmol) of *p*-bromostyrene were used. Chromatographic separation [silica gel, hexane/ethyl acetate (4:1/ v:v)] gave 1.0 g (30%) of **9b**. ^{1}H NMR ($CDCl_3$): δ 1.56 (s, 4 H, NH),

1.86 (dt, 8 H, CH_2CH$_2$NH), 1.95 (dt, 6 H, CH$_2$CH_2CH$_2$), 2.25 (t, 8 H, CH_2NH), 2.63 (m, 20 H, ArCH$_2$,), 5.25 (d, 1 H, CH=CH_2), 5.75 (d, 1 H, CH=CH_2), 6.72 (dd, 1 H, CH = CH$_2$), 6.83 (s, 6 H, ArH), 6.92 (s, 3 H, ArH), 7.24 (m, 40 H, ArH), 7.50 (d, 24 H, ArH). ^{13}C NMR (CDCl$_3$): δ 32.5, 33.0, 33.7, 35.2, 35.6, 43.4, 70.8, 112.8, 125.7, 125.8, 126.1, 127.7, 128.3, 128.5, 136.6, 142.0, 142.2, 146.2. FAB; *m/z* (%): 1657 (0.06) [M + H]$^+$. Anal. Calcd for $C_{123}H_{122}N_4$ (1656.3): C, 89.20; H, 7.42; N, 3.38. Found: C, 88.75; H, 7.35; N, 3.48.

3,5-Bis{3-[2-(trimethylsilyl)ethoxycarbonylamino]propyloxy}benzoic-*N*-hydroxysuccinimidyl Ester (10b). To a solution of **10a** (3.6 g, 6.45 mmol), in 225 mL of dry dichloromethane, were added 0.9 g (7.7 mmol) of *N*-hydroxysuccinimide and 1.65 g (8.0 mmol) of DCC. The mixture was stirred for 24 h at room temperature. The resulting precipitate was filtered off. Chromatographic separation [silica gel,hexane/ethyl acetate (2:1/(v:v)] gave 3.8 g of **10b** (89%) as a colorless solid. ^{1}H NMR (CDCl$_3$, 270 MHz): δ 0.00 (s, 18 H, TMS), 0.95 (t, 4 H, TMSCH$_2$), 1.92 (m, 4 H, OCH$_2$CH_2), 2.90 (s, 4 H, NHCOCH_2), 3.34 (t, 4 H, NHCH_2), 3.92 (t, 4 H, ArOCH$_2$), 4.10 (t, 4 H, OCH$_2$), 4.90 (br, 2 H, NH), 6.70 (s, 1 H, ArH), 7.20 (s, 2 H, ArH). ^{13}C NMR (CDCl$_3$, 62 MHz): δ −1.6 (TMS), 17.6, 25.5, 29.2, 37.9, 62.8, 65.9, 108.3, 108.6, 156.7, 159.9, 161.5, 169.1. MS (EI, 80 ev), *m/z* (%): 653.3 (0.63) [M$^+$]. Anal. Calcd for $C_{29}H_{47}N_3O_{10}Si_2$ (653.8): C, 53.27; H, 7.24; N, 6.42. Found: C, 53.21; H, 7.17; N, 6.34.

4-Allyl-{3,5-bis{3-{3,5-bis{3-{3,5-bis[3-[2-trimethylsilylethoxycarbonyamino]propyloxy]benzoylamino}propyl}benzylpropyl}benzylpropyl}benzene (11). To 0.8 g (0.77 mmol) of **8c** in 5 mL of methanol was added 2.9 g (4.4 mmol) of **10b**. The solution was stirred for 24 h at room temperature. Chromatographic separation [silica gel, hexane/ethyl acetate (1:1.6/v:v)] gave 1.2 g (57%) of **11** as a white solid. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 0.00 (s, 72 H, TMS), 0.92 (t, 16 H, TMSCH$_2$), 1.92 (br, 28 H, CH$_2$CH_2CH$_2$), 2.53 (br, 16 H, ArCH$_2$), 3.22 (br, 18 H, OCONHCH_2, CH_2CH=CH$_2$), 3.45 (t, 8 H, ArCONHCH_2), 3.84 (t, 16 H, ArOCH$_2$), 4.09 (t, 16 H, OCH_2-CH$_2$TMS), 5.00 (m, 2 H, CH=CH$_2$), 5.32 (s, 8 H, NH), 5.88(m, 1 H, CH=CH$_2$), 6.42 (s, 4 H, ArH), 6.78 (br, 17 H, ArH), 7.18 (s, 4 H, NH). ^{13}C NMR (CDCl$_3$, 125 MHz): δ −1.5, 17.5, 29.3, 30.5, 32.8, 35.1, 37.8, 39.5, 39.9, 62.6, 65.4, 104.0, 105.4, 115.4, 125.7, 125.9, 126.1, 136.5, 137.4, 139.6, 141.4, 142.0, 142.4, 156.8, 159.6, 167.1. FAB; *m/z* (%): 2737.0 (2.5) [M − H]$^+$. Anal. Calcd for $C_{139}H_{226}N_{12}O_{28}Si_8$ (2738.0): C, 60.97; H, 8.32; N, 6.13. Found: C, 60.19; H, 8.17; N, 5.91.

4-Vinyl{3,5-bis{3-{3,5-bis{3-{3,5-bis[3-[2-(trimethylsilyl)ethoxycarbonyamino]propyloxy]benzoylamino}propyl}benzyl}propyl}benzylpropyl}benzene (12). 12 was prepared by the same method as for **7a**, using 1.2 g (0.44 mmol) of **11**, 0.07 g (0.57 mmol) of 9-BBN, and 12 mL of dry THF. Subsequently, 5 mL of 1 M NaOH, 0.01 g of Pd(PPh$_3$)$_4$, and 0.28 g (1.5 mmol) of **6** were used. Chromatographic separation [silica gel, hexane/ethyl acetate (1:1.8/v:v)] gave 0.50 g (40%) of **12** as a white solid. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 0.00 (s, 72 H, TMS), 0.93 (t, 16 H, TMSCH$_2$), 1.90 (br, 30 H, CH$_2$CH_2-CH$_2$), 2.58 (br, 20 H, ArCH$_2$), 3.27 (t, 16 H, OCONHCH_2), 3.48 (t, 8 H, ArCONHCH_2), 3.89 (t, 16 H, ArOCH$_2$), 4.11 (t, 16 H, OCH_2CH$_2$TMS), 5.10 (br, 8 H, NH), 5.13 (d, 1 H, CH=CH$_2$), 5.18 (d, 1 H, CH=CH$_2$), 6.45 (s, 4 H, ArH), 6.65 (dd, 1 H, CH=CH$_2$) 6.68 (br, 17 H, ArH), 6.90 (br, 4 H, NH), 7.20 (AA′BB′, 4H, ArH). ^{13}C NMR (CDCl$_3$, 125 MHz): δ −1.5, 17.7, 29.3, 30.6, 32.9, 35.1, 35.3, 35.4, 37.9, 39.5, 62.8, 65.6, 104.1, 105.5, 112.8, 125.8, 126.0, 126.3, 128.5, 135.0, 136.5, 136.7, 141.4, 142.0, 142.7, 156.8, 159.7, 167.1. FAB: *m/z* (%): 2842.6 (1.0) [M+H]$^+$. Anal. Calcd for $C_{147}H_{234}N_{12}O_{28}Si_8$ (2841.6): C, 62.12; H, 8.30; N, 5.91. Found: C, 61.43; H, 8.12; N, 5.77.

Poly{vinyl[3,5-bis[3-[2-(trimethylsilyl)ethoxycarbonylamino]propyl]benzylpropyl]benzene} (13a). Polymerization was carried out in a sealed Schlenck tube under nitrogen atmosphere. See Table 1. From G-1 monomer **7a**: 80 mg of **7a,** 74 μL of a 0.05 M solution of AIBN in toluene, and 50 μL of toluene, were stirred at 55 °C for 48 h. The raw polymer was dissolved in 1 mL of THF, three times precipitated with methanol/water (4:1/v:v), and lyophilized from benzene. ^{1}H NMR (CDCl$_3$, 500 MHz): δ −0.15 to +0.15 (br, 18 H, TMS), 0.86−1.05 (br, 4 H, TMSCH_2), 1.05−1.50 (br, 2 H, CH$_2$), 1.50−1.92 (br, 6 H, ArCH$_2$CH_2), 2.15−2.65 (br, 9 H, ArCH$_2$, CH), 2.97−3.22 (br, 4 H, NHCH_2), 4.00−4.24 (br, 4 H, OCH$_2$), 5.02−5.30 (br, 2 H, NH), 6.02−6.48 (br, 2 H, ArH), 6.50−7.00 (br, 5 H, ArH). ^{13}C NMR (CDCl$_3$, 125 MHz): δ −1.50 (TMS), 17.7, 31.5, 32.8, 35.6, 40.4, 62.6, 125.7, 125.9, 126.2, 127.6, 141.4, 142.4, 156.9. Anal. Calcd for $(C_{35}H_{56}N_2O_4Si_2)_n$ (625.0)$_n$: C, 67.26, H, 9.03; N, 4.48. Found: C, 66.56; H, 8.58; N, 4.25.

Poly{4-Vinyl{3,5-bis[3-triphenylmethylaminopropyl]benzylpropyl}benzene} (13b) from G-1 Monomer 7b. A series of optimizations were done. To facilitate the experimental procedure the concentrations were not determined in mole-percent but in weight-percent. The concentrations ranged between 35 and 54% and were varied in steps of roughly 2−3%. For the run with optimum molar mass the experiment was repeated at a larger scale, and the concentration was then determined in mole-percent by taking the volume change into account associated with the dissolution process. The polymerizations at the higher concentrations did not proceed homogeneously.

13b was prepared by the same method as for **13a:** (Table 1, entry 2) 83 mg of **7b**, 60 μL of a 0.05 M solution of ^{t}BPB in toluene, and 65 μL of toluene; (Table 1, entry 3) 92 mg of **7b**, 53 μL of ^{t}BPB solution of diethyl ketone, and 66 μL of diethyl ketone. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 1.30−1.55 (br, 4 H, CH$_2$, NH); 1.55−1.90 (br, 6 H, ArCH$_2$CH_2), 2.00−2.21 (br, 4 H, NHCH_2), 2.21−2.67 (br, 9 H, ArCH$_2$, ArCH), 6.03−6.49 (br, 2 H, ArH), 6.49−6.90 (br, 5 H, ArH), 6.90−7.30 (br, 18 H, ArH), 7.32−7.51 (br, 12 H, ArH). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 32.5, 33.6, 35.3, 35.6, 43.4, 70.7, 125.8, 126.0, 127.8, 128.5, 142.1, 146.2. Anal. Calcd for $(C_{61}H_{60}N_2)_n$ (820.1): C, 89.27; H, 7.32; N, 3.41. Found: C, 88.19; H, 7.40; N, 2.91.

Poly{4-vinyl[3,5-[bis(3-aminopropyl)benzyl]propyl]benzene}−Bis(trifluoroacetic acid) (13c). A mixture of 0.5 g of **13b** and 0.3 mL of trifluoroacetic acid in 1 mL of methanol was stirred at 20 °C for 48 h. Subsequently, 2 mL of diethyl ether was added with stirring, and the mixture was centrifuged. After removal of the solvent, the residue was dried. This procedue was then repeated for one to two times. The residue was lyophilized from water under high vacuum. ^{1}H NMR ([D$_4$]-MeOH): δ 1.00−1.55 (br, 2 H, CH$_2$), 1.55−2.02 (br, 6 H, ArCH$_2$CH_2), 2.20−2.72 (br, 9 H, ArCH$_2$, CH), 2.72−2.95 (br, 4 H, NH$_3^+$CH_2), 6.02−6.48 (br, 2 H, ArH), 6.50−7.00 (br, 5 H, ArH). ^{13}C NMR ([D$_4$]MeOH): δ 30.3, 31.4, 33.5, 34.5, 36.5, 40.3, 41.3, 118.2 (q,CF$_3$), 126.9, 127.7, 128.8, 142.0, 144.3, 163.0 (q, CF$_3$*C*OO). Anal. Calcd for $(C_{27}H_{34}N_2O_4F_6)_n$ (564.6)$_n$: C: 57.44; H, 6.07; N, 4.94. Found: C, 56.63; H, 5.82; N, 4.57.

Poly{4-vinyl{3,5-bis{3-{3,5-bis[3-[2-(trimethylsilyl)ethoxycarbonylamino]propyl}benzyl}propyl}benzene} (14a) from G-2 Monomer 9a. 14a was prepared by the same method as for **13a**, using 98 mg of **9a**, 42 μL of the ^{t}BPB solution in toluene, and 35 μL of toluene. ^{1}H NMR (CDCl$_3$, 500 MHz): δ −0.15 to +0.15 (br, 36H, TMS), 0.86−1.04 (br, 8H, TMSCH$_2$), 1.35−1.74 (br, 10H, ArCH$_2$CH_2, CH$_2$), 1.74−2.05 (br, 6H, ArCH$_2$CH_2), 2.20−2.71 (br, 21H, ArCH$_2$, ArCH), 2.90−3.22 (br, 8H, NHCH$_2$), 4.00−4.21 (br, 8H, OCH$_2$), 5.02−5.45 (br, 4H, NH), 6.00−6.48 (br, 2H, ArH), 6.50−6.96 (br, 11H, ArH). ^{13}C NMR (CDCl$_3$, 125 MHz): δ −1.5 (TMS), 17.7, 31.4, 32.8, 33.1, 35.6, 40.3, 62.6, 125.8, 126.0, 127.4, 141.4, 141.9, 142.3, 156.9. Anal. Calcd for $(C_{71}H_{114}N_4O_8Si_4)_n$ (1264.0)$_n$: C, 67.46; H, 9.09; N, 4.43. Found: C, 66.67; H, 8.82; N, 4.28.

Poly{4-vinyl{3,5-bis{3-{3,5-bis[3-triphenylmethylaminopropyl]benzyl}propyl}benzylpropyl}benzene} (14b) from G-2 monomer 9b. 14b was prepared by the same method as for **13a**, using 102 mg of **9b**, 36 μL of the ^{t}BPB solution in diethyl ketone, and 41 μL of diethyl ketone. ^{1}H NMR (CDCl$_3$, 270 MHz): δ 1.30−1.60 (br, 6 H, NH, CH$_2$), 1.60−1.92 (br, 14 H, CH$_2$), 1.92−2.26 (br, 8 H, NHCH_2), 2.26−2.82 (br, 21 H, ArCH$_2$, ArCH), 6.38−6.78 (br, 13 H, ArH), 6.78−7.20 (br, 36 H, ArH), 7.20−7.62 (br, 24 H, ArH)**.** ^{13}C NMR: δ 32.5, 33.1, 33.7, 35.7, 43.5, 70.8, 126.1, 127.7, 128.6, 142.1, 146.2. Anal. Calcd for $C_{123}H_{122}N_4$ (1656.3)n: C, 89.20; H, 7.42; N, 3.38. Found: C, 88.81; H, 7.51; N, 3.55.

Poly{4-vinyl{3,5-bis[3,5-bis[3-aminopropyl]benzylpropyl]benzylpropyl}benzene}−Tetrakis(trifluoroace-

tic acid) (14c) from polymer 14a. ^{1}H NMR ([D$_4$]MeOH): δ 1.35−2.10 (br, 16 H, ArCH$_2$C*H*$_2$, CH$_2$), 2.10−2.70 (br, 21 H, ArCH$_2$, ArCH), 2.71−3.05 (br, 8 H, NH$_3^+$CH$_2$), 5.70−6.50 (br, 2 H, ArH), 6.50−7.10 (br, 11 H, ArH). ^{13}C NMR ([D$_4$]MeOH): δ 30.2, 33.4, 34.7, 36.7, 40.2, 118.0 (q, CF$_3$), 126.9, 127.6, 142.0, 143.4, 144.3, 162.2 (q, CF$_3$*C*OO).

Poly{4-vinyl-3,5-bis{3-{3,5-bis[3-[2-(trimethlsilyl)-ethoxycarbonylamino]propyloxy]benzoylamino}propyl}-benzylpropyl}benzene} (15). To a solution of 28 mg of **13c** in 2 mL of methanol were added 0.20 g (2.0 mmol) of triethylamine and 0.123 g (0.19 mmol) of **10b.** After the mixture was stirred for 3 h at room temperature, 2 mL of dichloromethane was added. The resulting mixture was stirred for 48 h. After removal of the solvents, the residue was dissolved in 2 mL of THF and precipitated four times into methanol/water (4:1/v:v) and then lyophilized from benzene. ^{1}H NMR (CDCl$_3$, 500 MHz): δ −0.05 (br, 36 H, TMS), 0.80−1.02 (8 H, TMSCH$_2$), 1.28−2.03 (br, 16 H, CH$_2$C*H*$_2$CH$_2$, CH$_2$), 2.03−2.62 (br, 9 H, ArCH$_2$, CH), 2.90−3.48 (br, 12 H, NHC*H*$_2$), 3.48−3.91 (br, 8 H, ArOCH$_2$), 3.91−4.22 (br, 8 H, OCH$_2$), 5.41−5.73 (br, 4 H, NH), 6.30−6.50 (br, 4 H, ArH), 6.50−7.12 (br, 9 H, ArH), 7.60−8.32 (br, 2 H, NH). ^{13}C NMR (CDCl$_3$): δ −1.5 (TMS), 17.7 (TMSCH$_2$), 29.3, 30.7, 33.0, 37.9, 39.9 (NHCH$_2$), 62.7, 65.5, 104.3, 105.6, 126.1, 136.5, 141.3, 157.0 (OAr), 159.7 (NHCOO), 167.5 (CONH). Anal. Calcd for $(C_{73}H_{116}N_6O_{14}Si_4)_n$ $(1414.1)_n$: C, 62.00; H, 8.27; N, 5.94. Found: C, 61.02; H, 8.04; N, 5.70.

Poly{4-Vinyl{3,5-bis{3-{3,5-bis{3-{3,5-bis[3-[2-trimethylsilylethoxycarbonylamino]propyloxy]benzoylamino}propyl}benzyl}propyl}benzylpropyl}benzene} (17a) from G-3 Monomer 12. 17a was prepared by the same method as for **13a**, using 140 mg of **12**, 33 μL of the ^{t}BPB solution in toluene, and 36 μL of toluene.^{1}H NMR (CDCl$_3$, 500 MHz): δ −0.05 (br, 72 H, TMS), 0.80−1.00 (br, 1 H, TMSCH$_2$), 1.20−2.00 (br, 32 H, CH$_2$C*H*$_2$CH$_2$, CH$_2$), 2.00−2.80 (br, 21 H, ArCH$_2$, CH), 2.85−3.47 (br, 26 H, OCONHC*H*$_2$, ArCONHC*H*$_2$), 3.48−3.90 (br, 16 H, ArOCH$_2$), 3.90−4.25 (br, 16 H, OC*H*$_2$CH$_2$TMS), 5.00−5.87(br, 8 H, NH), 6.10−6.46 (br, 6 H, ArH), 6.46−7.12 (br, 17 H, ArH), 7.40−8.30 (br, 4 H, NH). ^{13}C NMR (CDCl$_3$, 125 MHz): δ − 1.5, 17.7, 29.3, 30.6, 32.9, 35.4, 37.9, 39.5, 62.7, 63.6, 65.5, 104.1, 105.7, 126.3, 126.9, 127,9, 136.5, 141.4, 142.0, 142.4, 157.0, 159.7, 167.4. Anal. Calcd for $(C_{147}H_{234}N_{12}O_{28}Si_8)_n$ $(2841.6)_n$: C, 62.12; H, 8.30; N, 5.91. Found: C, 61.40; H, 8.11; N, 5.62.

Poly{4-Vinyl{3,5-bis{3-{3,5-bis{3-{3,5-bis[3-[2-trimethylsilylethoxycarbonyamino]propyloxy]benzoylamino}propyl}benzyl}propyl}benzylpropyl}benzene} (17a). 17a was prepared by the same method as for **13c** + **10b**, using 55 mg of **13c**, 0.1 mL of triethylamine, 0.23 g (0.36 mmol) of **10b**, and 2 mL of methanol. Subsequently, 2 mL of dichloromethane was added. ^{1}H NMR (CDCl$_3$, 500 MHz): δ −0.05 (br, 72 H, TMS), 0.80−1.00 (br, 18 H, TMSCH$_2$, CH$_2$), 1.20−2.00 (br, 32 H, CH$_2$C*H*$_2$CH$_2$, CH), 2.00−2.80 (br, 21 H, ArCH$_2$, CH), 2.85−3.47 (br, 26 H, OCONHC*H*$_2$, ArCONHC*H*$_2$), 3.48−3.90 (br, 16 H, ArOCH$_2$), 3.90−4.25 (br, 16 H, OC*H*$_2$CH$_2$TMS), 5.00−5.87 (br, 8 H, NH), 6.10−6.46 (br, 6 H, ArH), 6.46−7.12 (br, 17 H, ArH), 7.40−8.30 (br, 4 H, NH). ^{13}C NMR (CDCl$_3$, 125 MHz): δ − 1.5, 17.7, 29.3, 30.6, 32.9, 35.4, 37.9, 39.5, 62.7, 63.6, 65.5, 104.1, 105.7, 126.3, 126.9, 127,9, 136.5, 141.4, 142.0, 142.4, 157.0, 159.7, 167.4. Anal. Calcd for $(C_{147}H_{234}N_{12}O_{28}Si_8)_n$ $(2841.6)_n$: C, 62.12; H, 8.30; N, 5.91. Found: C, 61.94; H, 8.11; N, 6.00.

Poly{4-Vinyl{3,5-bis{3-{3,5-bis{3-{3,5-bis[3-aminopropyloxy]benzoylamino}propyl}benzyl}propyl}benzylpropyl}benzene}−Octakis(trifluoroacetic acid) (17b) From G-3 Polymer *mm*-17a. ^{1}H NMR ([D$_4$]CH$_3$OH): δ 1.43−1.92 (br, 16 H, ArCH$_2$C*H*$_2$, CH$_2$), 1.92−2.21 (br, 16 H, OCH$_2$C*H*$_2$CH$_2$), 2.21−2.80 (br, 20 H, ArC*H*$_2$, CH), 2.90−3.17 (br, 16 H, C*H*$_2$-NH$_3^+$), 3.17−3.32 (br, 8 H, C*H*$_2$NHCO), 3.63−4.22 (br, 16 H, OC*H*$_2$), 6.30−6.84 (br, 14 H, ArH), 6.84−7.15 (br, 11 H, ArH). ^{13}C NMR: δ 28.2, 32.0, 34.4, 36.7, 38.3, 41.0, 42.0, 66.4, 105.6, 107.2, 118.2 (q, CF$_3$), 127.4, 128.6, 129.3, 137.7, 142.1, 142.9, 143.4, 143.8, 161.1, 162.6, 163.0, 163.2, 169.5. Anal. Calcd for $(C_{115}H_{146}N_{12}O_{28}F_{24})_n$ (2600.4): C, 53.13; H, 5.66; N, 6.46. Found: C, 52.49; H, 6.21; N, 7.58

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