Dendronized Polystyrenes with Hydroxy and Amino Groups in the Periphery

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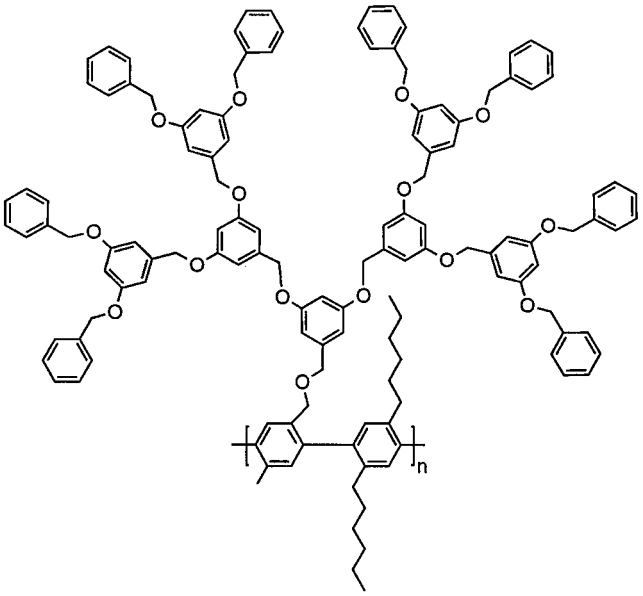
Introduction

During the last years particular interest in dendrimers arose, which do not have a spherical[1] but rather a cylindrical shape.[2] First attempts in this direction were filed in a U.S. patent in 1987 by Tomalia et al., where the divergent synthesis of dendrimers consisting of a poly(amidoamine) dendritic layer attached to a poly(ethyleneimine) core is described.[3] Recently, Percec et al. described the induction of shape control of dendronized polymers depending on the degree of polymerization leading to macromolecules with a cylindrical shape in the solid state obtained by the polymerization of second-generation dendronized methacrylates and styrenes.[4] We presently aim at the controlled synthesis of dendronized polymers which may be considered as cylindrical molecular objects in the nanometer range whose shape and dimensions are independent of the surrounding medium.[2] In this context we have reported the synthesis of polymers **1**[5] and **2**[6] carrying third generation dendrons on each repeat unit (Figure 1). Scanning force microscopical (SFM) studies of **2** adsorbed on highly oriented pyrolytic graphite, small-angle neutron-scattering (SANS) experiments in deuterio benzene and molecular modeling simulations provided evidence that **2** is an unusually rigid polymer.[7] Its backbone is stretched out and a cylindrical "surface" can be assigned to it. One of the next logical steps within this project is to try to introduce functional groups[8] at this "surface". This would allow one to engineer the properties of these unusually shaped macromolecules.

Here, we report some steps toward this goal which comprise of (a) the synthesis of new amino-terminated dendrons with orthogonally protected functional groups at the focal point (methyl ester) and in the periphery (trimethylsilyl ethoxycarbonyl, TEOC), (b) their attachment to a styrene derivative as well as that of some previously reported dendrons to yield polymerizable (dendritic) macromonomers, (c) the polymerization of the obtained monomers under high-concentration conditions, and (d) the deprotection of the resulting polymers at their peripherial functional groups.

Results and Discussion

It is sometimes difficult to predict the propensity of vinyl macromonomers to undergo polymerization.[9] Many factors including concentration, steric demand of the substituent, and solvent/monomer interaction play a role. The project was therefore approached by testing a variety of dendronized styrene monomers with first-(G-1) and second-(G-2) generation dendrons. Here, we give a short account of the most successful ones, the G-1 styrenes **9** and the G-2 styrenes **10**, which were obtained by reacting *p*-aminomethylstyrene **8** with dendrons **6a**, **6c**, **7a**, and **7c** (Figure 2).[10] These dendrons are characterized by amino or hydroxy functions in the periphery and carboxylic acid function at the focal point. The peripherial functions are protected by either tetrahydropyranyl (THP) (**6a**, **7a**) or TEOC protective groups (**6c**, **7c**).



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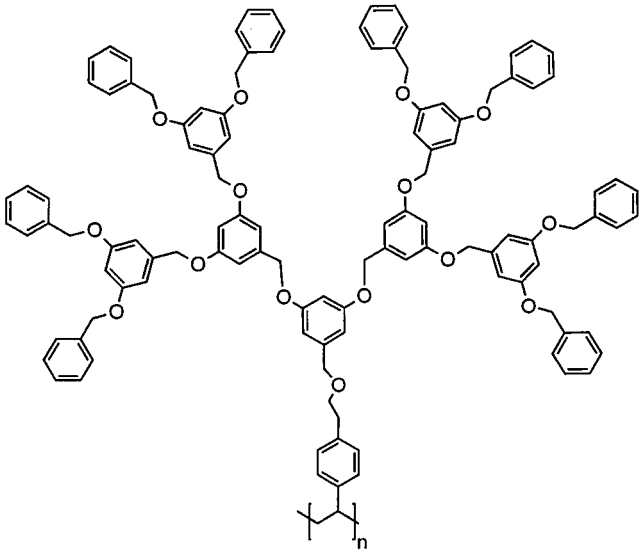

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Figure 1. Structures of G-3 poly(*p*-phenylene) **1** and G-3 polystyrene **2**.

The synthesis of dendrons **6a** and **7a** has already been reported;[11] the one of **6c** and **7c** is shown in Scheme 1. It starts with the synthesis of the protection reagent, trimethylsilylethyl chloroformate,[12] from trimethylsilylethanol **3** and phosgene. The in situ reaction of the chloroformiate formed and 3-chloropropylamine hydrochloride gave **4**. The TEOC-protected G-1 dendron **6b** was obtained from **4** and methyl 3,5-dihydroxybenzoate

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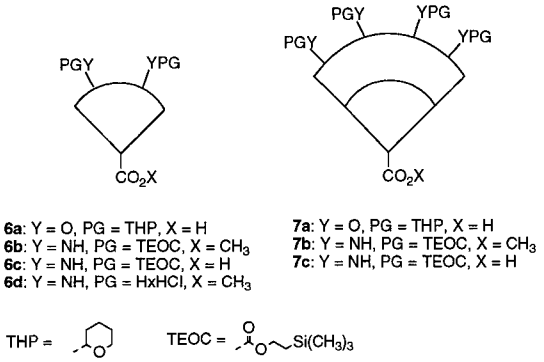
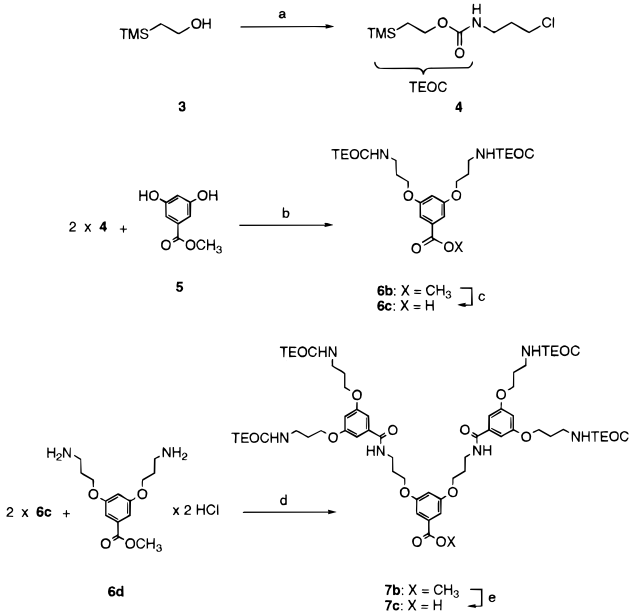


Figure 2. Schematic structures of G-1 dendrons **6** and G-2 dendrons **7**.

Scheme 1. Synthesis of G-1 Dendrons 6 and G-2 Dendrons 7[a]

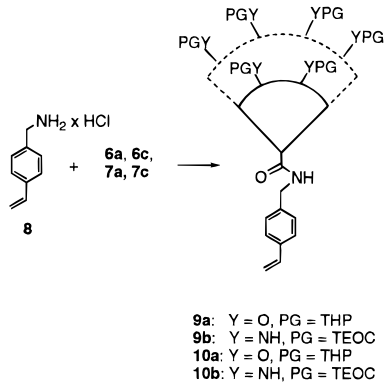


[a] Reagents and conditions: (a) 1. K_2CO_3, $COCl_2$, toluene, 0 °C, 30 min; 2. 3-chloropropylamine hydrochloride, KOH, THF/water, 20 °C, 20 H, (65%); (b) K_2CO_3, 18-C-6, tetrabutyl ammonium iodide, diethyl ketone, reflux, 20 h (85%); (c) KOH, methanol/water, reflux, 5 h (95%); (d) 1. **6c**, CDI, THF, 40 °C, 24 h; 2. **6d**, DBU, CH_2Cl_2, 0 °C, 24 h, (65%); (e) KOH, methanol/water, reflux, 8 h, (80%).

5[13] on the 30 g scale in 85% yield. Methyl ester **6b** was selectively saponified with potassium hydroxide in methanol/water to give the corresponding carboxylic acid **6c** in 95% yield. A combination of 2 equiv of acid **6c** with G-1 dendron **6d**,[14] which carries two free amino functions, gave the second-generation dendron **7b**. This amide coupling was achieved by CDI[15] as the activation agent on the 20 g scale in 65% yield. Saponification of **7b** with potassium hydroxide proceeded cleanly and yielded G-2 acid **7c** (10 g, 80%).

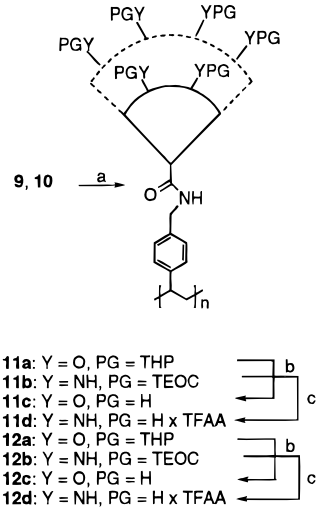
The peripherially THP-protected hydroxy-functionalized (**6a**, **7a**), as well as the TEOC-protected amino-functionalized, dendron acids (**6c**, **7c**) were attached to 4-aminomethylstyrene **8**[16] to give the corresponding macromonomers **9** (G-1) and **10** (G-2) (Scheme 2). In all cases amide coupling was done by the convenient EDC/HOBT method.[17] The syntheses were carried out on the 4−7 g scale and gave the monomers in yields from 65% to 85% after purification by simple column chromatography (filtration). The structures of all macromonomers were established by ^{1}H- and ^{13}C NMR spectroscopy,

Scheme 2. Synthesis of G-1 Macromonomers 9 and G-2 Macromonomers 10[a]



[a] Reagents and conditions: 1. dendron acid, HOBT, CH_2Cl_2, 0 °C, 1 h, 2. EDC, 1 h, 3. **8**, DBU, 25 °C, 20 h.

Scheme 3. Polymerization of Macromonomers 9 (G-1) and 10 (G-2) and Deprotection of the Obtained Polymers 11 (G-1) and 12 (G-2)[a]



[a] Reagents and conditions: (a) see Table 1; (b) 1. THP-protected polymer, THF, HCl (2% in methanol), r.t., 5 h; 2. DMF, HCl (2% in methanol), r.t., 20 h; (c) TEOC-protected polymer, trifluoroacetic acid, r.t., 20 h.

FAB mass spectrometry, and correct data from elemental analysis.

The results of the radical polymerization of styrene monomers **9** and **10** are shown in Table 1. Molecular weights were determined by gel permeation chromatography (GPC) with tetrahydrofuran (THF) as the eluent and polystyrene standard.[18] Polymerizations were carried out in relatively concentrated toluene solutions (0.80−1.00 mol/L). Lower concentrations led to a sharp decrease in molecular weights (see also ref 9). Higher concentrations were not applied because of insufficient monomer solubility. The highest monomer concentration allowing the reaction medium to be homogeneous at least in the initial phase could be achieved with the TEOC-protected G-1 monomer **9b**. Interestingly, this macromonomer gave the highest molecular weight. The relatively mild conditions applied in the polymerization of G-1 monomers were not successful for G-2. Table 1 gives minimum temperatures required for the polymerization of the latter to achieve reasonable molecular weights.[19] Despite those more drastic conditions both molecular weights and yields of G-2 polymers **12a** and **12b** are lower than those of G-1

Table 1. Some Synthetic Details and Results of Polymerizations Carried out with Macromonomers 9 (G-1) and 10 (G -2)

polymer	Y	PG	monomer conc. [mol/L]	initiator (3 mol %)	T [°C]	yield[d] [%]	M_n[e] [$\times 10^4$]	P_n	M_w/M_n
11a	O	THP	0.80	AIBN[a]	50	90	7.3	132	2.5
11b	NH	TEOC	1.00	AIBN	50	97	11.1	166	2.9
12a	O	THP	0.80	^{t}BPB[b]	80	86	4.9	40	1.6
12b	NH	TEOC	0.80	BPO[c]	60	79	4.8	40	2.2

[a] 2,2′-Azoisobutyronitril. [b] *tert*-Butylperoxybenzoate. [c] Benzoylperoxide. [d] Determined by ^{1}H NMR spectra of the crude product. [e] Determined for crude products by GPC with THF as the eluent and polystyrene standard.

polymers **11a** and **11b** which seems to reflect the steric hindrance imparted by the larger dendrons (Scheme 3).

Deprotection of THP (**11a**, **12a**) was accomplished in two consecutive steps with diluted hydrochloric acid in methanol/THF and methanol/DMF (*N*,*N*-dimethylformamide), respectively. The achieved degrees of deprotection were virtually quantitative (>98%, 500 MHz NMR). The obtained polymers, carrying two (**11c**) or four hydroxy functionalities (**12c**) per repeating unit, were characterized by ^{1}H and ^{13}C NMR spectroscopy, and thermogravimetric analysis (TGA). Unfortunately, we were not able to get correct data from elemental analysis. The polymers could not be dried completely even when exposed to high vacuum at elevated temperatures.

Deprotection of the TEOC polymers **11b** and **12b** was done by treatment of the neat material with trifluoroacetic acid. The deprotected polymers with two (**11d**) or four quaternized amino functions (**12d**) per repeating unit were isolated as trifluoroacetates and were obtained as analytically pure materials after lyophilization from water. They were characterized by ^{1}H and ^{13}C NMR spectroscopy, correct data from elemental analysis, TGA, and viscometry. The ^{1}H NMR spectra of the G-2 monomer **10b**, protected polymer **12b**, and deprotected amine-functionalized polymer **12d** are compared in Figure 3. In the latter spectrum the signals for the TEOC protective group (marked with ° in spectra (a) and (b)) have completely vanished, illustrating the efficiency of the deprotection process. Additionally, the NMR spectra did not give any indication of decomposition under deprotection conditions, neither concerning the skeletons of the dendrons nor their attachment to the polymeric backbone (core). The spectrum of deprotected **12d** (c) shows shoulders and additional signals at $\delta = 1.8$, 3.4, and 6.4 which are due to comparable protons positioned in different generations. As in the macromonomer (a) but in contrast to the protected polymer (b), they do not absorb isochronically. Both ammonium polymers **11d** and **12d** were examined in viscometry experiments, which gave a typical increase of the reduced viscosity with decreasing concentrations (polyelectrolyte effect).[20]

The solubility of the obtained polymers is strongly influenced by the nature of their functionalization. THP and TEOC-protected polymers (both G-1 and G-2) are completely soluble in benzene, chloroform, and THF, but not in hexane or water. In contrast, the highly polar ammonium-functionalized **11d** and **12d** are soluble in water, methanol, and DMF, while the hydroxy polymers **11c** and **12c** are soluble in DMF and insoluble in water and methanol. Hydroxy- and amine-functionalized polymers tend to form hydrogen bonds, which can go as far as that; once a polymer is dried passed a certain degree, it cannot be redissolved.

Conclusions

In summary, styrenes with first- and second-generation dendrons carrying protected functional groups in the periphery can be polymerized to high-molecular-weight linear polymers. Deprotection of these easily available polymers proceeds quantitatively and provides access to a new type of polyelectrolytes. This work constitutes a step toward surface-functionalized, cylindrical nano objects.

Experimental Section

General Procedures. All reagents were purchased from Fluka or Aldrich and used without further purification. The following compounds were prepared according to literature methods: *p*-aminomethylstyrene hydrochloride (**8**)[16], methyl 3,5-dihydroxybenzoate (**5**),[13] **6d**,[14] and **6a**, **7a**.[11] All solvents were dried under standard conditions. All reactions were carried out under nitrogen. NMR spectra were obtained on a Bruker 500 spectrometer (500 MHz) at room temperature. Gel permeation chromatography (GPC) measurements were carried out using a Waters ultra styragel linear column (r.i. and u.v. (230 nm) detection; polystyrene standard; THF eluent). The thermal analyses were pereformed on a Netzsch TG 209 (thermogravimetric analysis (TGA)). Viscometry measurements of **11d** and **12d** were performed in water at 25.0 °C using an automatic Schott AVS 360 instrument (Ubbelohde Viscometers).

3-[2-(Trimethylsilyl)ethoxycarbonylamino]propyl Chloride (4). *All operations were performed in a well-ventilated hood.* To a solution of 10.6 g (90 mmol) of 2-trimethylsilylethanol (**3**) and 130 g (220 mmol) of anhydrous potassium carbonate in 100 mL of toluene was added dropwise 57 mL of a 20% solution of phosgene (99 mmol) in toluene and stirred for a 0.5 h at 0 °C. After being warmed to room temperature, the solution was stirred for another hour. Subsequently, the solvent was removed in a vacuum at a bath temperature less than 40 °C *with a closed hood*. A suspension of the raw oil, 12.8 g (98 mmol) of 3-chloropropylamine hydrochloride dissolved in 150 mL of THF and 10.6 g (189 mmol) of potassium hydroxide dissolved in 100 mL of water was stirred at 20 °C for 20 h. The organic layer was washed with water (3 × 150 mL) and dried with magnesium sulfate. Distillation (90 °C, 10^{-3} mbar) gave 14.6 g (65%) of **4**. ^{1}H NMR ($CDCl_3$): δ 0.0 (s, 9H, TMS), 0.9 (t, 2H, TMSCH_2), 2.0 (q, 2H, CH_2), 3.3 (q, 2H, NHCH_2), 3.6 (t, 2H, CH_2Cl), 4.1 (t, 2H, OCH_2), 4.8 (br, 1H, NH). ^{13}C NMR ($CDCl_3$): δ −1.5 (TMS), 17.7 (TMSCH_2), 32.4 (CH_2), 38.1 (CH_2−NH), 42.2 (CH_2Cl), 63.0 (OCH_2), 156.8 (NHCOO). MS (70 eV) *m*/*z* (%): 237 (0.2) [M^+], 222 (2) (HRMS: calcd, 222.07171; found, 222.07354) [$M^+ - CH_3$]. Calcd for $C_9H_{20}NO_2SiCl$ (237.8): C, 45.46; H, 8.48; N, 5.89. Found: C, 45.52; H, 8.32; N, 5.39.

Methyl 3,5-Bis{3-[2-(trimethylsilyl)ethoxycarbonylamino]propyloxy}benzoate (6b). A solution of 30.5 g (128 mmol) of **4**, 10.8 g (64 mmol) of methyl 3,5-dihydroxybenzoate (**5**), 28 g (0.2 mol) of potassium carbonate, 2 g of 18-crown-6 and 2 g of tetrabutylammonium iodide in 500 mL of diethyl ketone was refluxed for 20 h. The solution was washed with water (3 × 150 mL) and dried with magnesium sulfate. Chromatographic separation (silica gel, hexane/ethyl acetate (2:1/v:v)) gave 31.2 g (85%) of **6b** as a viscous oil. ^{1}H NMR ($CDCl_3$): δ 0.0 (s, 18H, TMS), 0.9 (t, 4H, TMSCH_2), 2.0 (m,

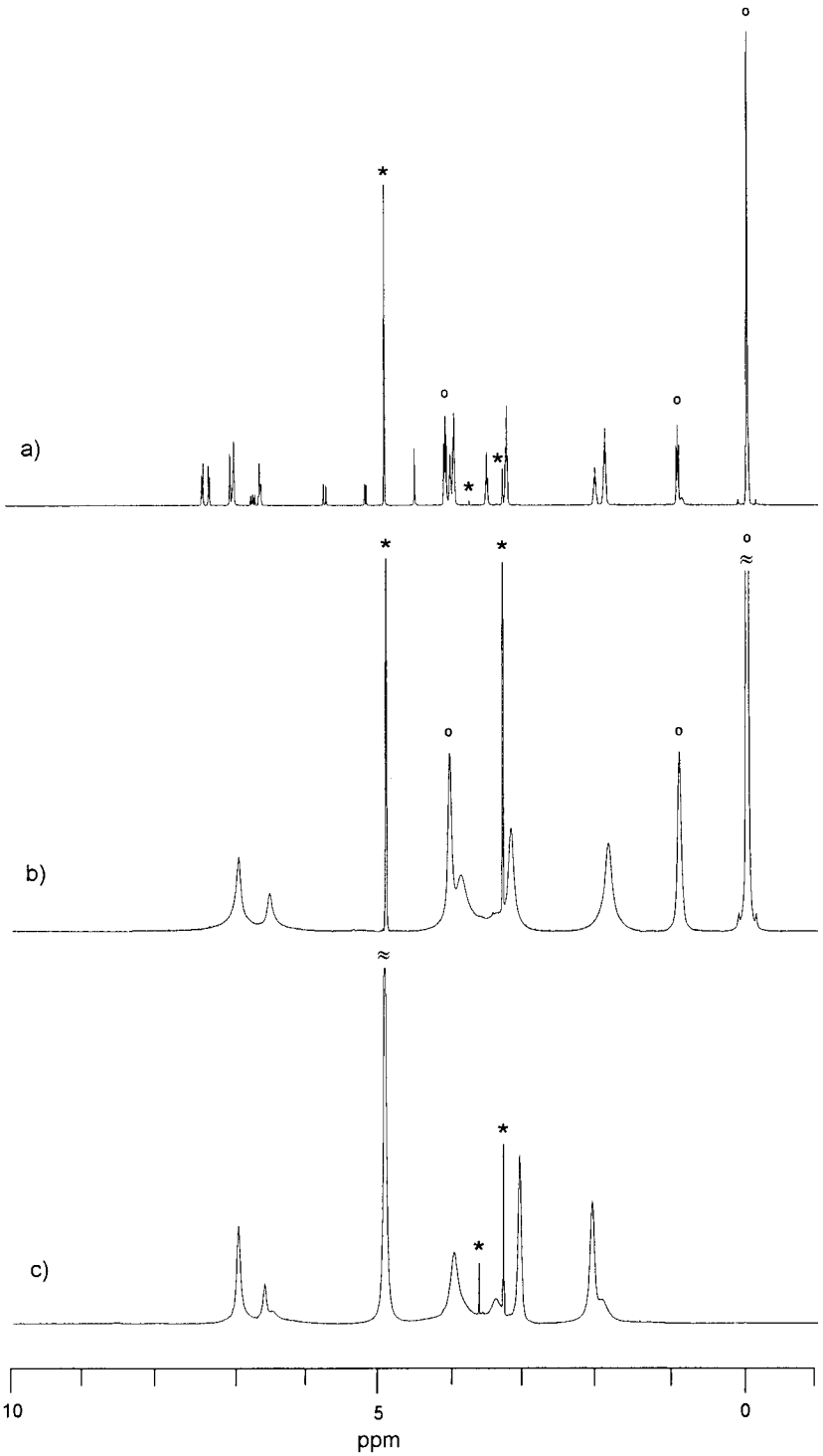


Figure 3. ^{1}H NMR spectra of TEOC-protected G-2 macromonomer **10b** (a), TEOC-protected polymer **12b** (b), and peripherially deprotected amino polymer **12d** (c). All spectra (500 MHz) at room temperature in [D_4] methanol. Signals for TEOC protective group (°) and solvents (*) are marked.

4H, CH_2), 3.3 (m, 4H, NHCH_2), 3.9 (s, 3H, CH_3), 4.0 (t, 4H, ArOCH_2), 4.1 (t, 4H, OCH_2), 4.9 (br, 2H, NH), 6.6 (t, 1H, ArH), 7.1 (d, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ −1.5 (TMS), 17.7 ($TMSCH_2$), 29.4 (CH_2), 38.2 ($NHCH_2$), 52.2 (CH_3), 62.9, 65.9 (OCH_2), 106.5, 107.8, 131.9 (Ar), 156.8 (NHCOO), 159.7 (OAr), 166.6 (CONH). MS (70 eV) *m*/*z* (%): 570 (0.1) [M^+], 334 (4.6) [M^+ − 2TMS − C_2H_4O]. Calcd for $C_{26}H_{46}N_2O_8Si_2$ (570.8): C, 54.71; H, 8.12; N, 4.91. Found: C, 54.43; H, 7.93; N, 4.71.

3,5-Bis{3-[2-(trimethylsilyl)ethoxycarbonylamino]-propyloxy}benzoic Acid (6c). A solution of 25 g (44 mmol) of **6b** and 7.4 g (130 mmol) of potassium hydroxide in 250 mL of methanol/water (1.1/v:v) was refluxed for 5 h. After removal of the solvent, the oily residue was dissolved in ethyl acetate, washed with a 10% citric acid solution in water (1 × 100 mL) and then water (3 × 100 mL), and dried with magnesium sulfate. The removal of the solvent gave 23.3 g (95%) of **6c** as a viscous oil. ^{1}H NMR ($CDCl_3$): δ 0.0 (s, 18H, TMS), 0.9 (t, 4H, TMSCH_2), 2.0 (m, 4H, CH_2), 3.3 (m, 4H, NHCH_2), 4.0 (t, 4H, ArOCH_2), 4.1 (t, 4H, OCH_2), 5.0 (br, 2H, NH), 6.6 (t, 1H, ArH), 7.2 (d, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ −1.5 (TMS), 17.7 ($TMSCH_2$), 29.3 (CH_2), 38.2 ($NHCH_2$), 63.0, 65.9 (OCH_2), 107.0, 108.2, 131.7 (Ar), 156.9 (NHCOO), 159.7 (OAr), 166.5 (CONH). MS (70 eV) *m*/*z* (%): 556 (5.4) [M^+]. Calcd for $C_{25}H_{44}N_2O_8Si_2$ (556.8): C, 53.93; H, 7.96; N, 5.03. Found: C, 53.65; H, 7.78; N, 4.69.

Methyl 3,5-Bis{3-{3,5-bis[3-[2-(trimethylsilyl)ethoxycarbonylamino]propyloxy]benzoylamino}propyloxy}benzoate (7b). A solution of 28.1 g (50.5 mmol) of **6c** and 9 g (55 mmol) of *N*,*N*′-carbonyldiimidazole in 300 mL of dry THF was stirred at 40 °C for 24 h. After the solution was cooled to 0 °C and 1 mL of water was added to a solution of 9 g (25.2 mmol) of methyl 3,5-bis(3-aminopropyloxy)benzoate · 2HCl (**6d**) and 7.8 g (52 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-en (DBU) in 200 mL of dry methylene chloride was added and stirred for a further 24 h. The solution was washed with water (3 × 100 mL) and dried with magnesium sulfate. Chromatographic separation (silica gel, hexane/ethyl acetate (1:2/v:v)) gave 20 g (65%) of **7b** as colorless crystals, mp 55−57 °C. ^{1}H NMR ($CDCl_3$): δ 0.0 (s, 36H, TMS), 0.9 (t, 8H, TMSCH_2), 1.8 (q, 8H, CH_2), 2.1 (q, 4H, CH_2), 3.3 (q, 8H, NHCH_2), 3.5 (q, 4H, NHCH_2), 3.8 (s, 3H, CH_3), 3.9 (t, 8H, ArOCH_2), 4.1 (t, 4H, ArOCH_2), 4.2 (t, 8H, OCH_2), 5.0 (br, 4H, NH), 6.5 (t, 2H, ArH), 6.6 (t, 1H, ArH), 6.9 (m, 6H, ArH, NH), 7.1 (d, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ −1.5 (TMS), 17.8 (TMSCH_2), 28.9, 29.5 (CH_2), 37.8, 38.2 ($NHCH_2$), 52.2 (CH_3), 62.9, 65.9, 66.7 (OCH_2), 104.6, 105.7, 106.8, 108.0, 132.1, 136.8 (Ar), 156.9 (NHCOO), 159.7, 160.0 (OAr), 166.6, 167.2 (CONH). FAB-MS *m*/*z* (%): 1384.0 (1.3) [M^+ + Na]. Calcd for $C_{64}H_{106}N_6O_{18}Si_4$ (1359.9): C, 56.53; H, 7.86; N, 6.18. Found: C, 56.27; H, 7.48; N, 6.23.

3,5-Bis{3-{3,5-bis[3-[2-(trimethylsilyl)ethoxycarbonylamino]propyloxy]benzoylamino}propyloxy}benzoic Acid (7c). A solution of 13.1 g (9.6 mmol) of **7b** and 1.6 g (29 mmol) of potassium hydroxide in 150 mL of methanol/water (1.1/v:v) was refluxed for 8 h. After removal of the solvent, the oily residue was dissolved in ethyl acetate, washed with a 10% citric acid solution in water (1 × 50 mL) and then water (3 × 60 mL), and dried with magnesium sulfate. The removal of the solvent gave 10.3 g (80%) of **7c** as colorless crystals, mp 81−83 °C. ^{1}H NMR ([D_4] MeOH): δ 0.0 (s, 36H, TMS), 0.9 (br, 8H, TMSCH_2), 1.8 (br, 8H, CH_2), 2.0 (br, 4H, CH_2), 3.1 (br, 8H, NHCH_2), 3.4 (br, 4H, NHCH_2), 3.8 (br, 12H, ArOCH_2), 4.0 (br, 8H, OCH_2), 4.7 (br, 4H, NH), 6.5 (br, 3H, ArH), 6.8 (br, 6H, ArH), 7.2 (br, 2H, NH). ^{13}C NMR ([D_4] MeOH): δ −1.2 (TMS), 18.6 (TMSCH_2), 30.1, 30.7 (CH_2), 38.7, 39.3 ($NHCH_2$), 63.8, 64.4, 66.8 (OCH_2), 105.6, 107.0, 109.2, 136.1, 137.5 (Ar), 159.1 (NHCOO), 160.7, 161.4 (OAr), 173.6, 174.7 (CONH). FAB−MS *m*/*z* (%): 1343 (88) [M^- − H]. Calcd for $C_{63}H_{104}N_6O_{18}Si_4$ (1345.9): C, 56.22; H, 7.79; N, 6.24. Found: C, 55.06; H, 7.25; N, 5.79.

General Procedure for Macromonomer Preparation. To a solution of 12.2 mmol of protected dendron acid in 100 mL of dry methylene chloride was added 1.8 g (12.2 mmol) of 1-hydroxybenzotriazole (HOBt) at 0 °C and stirred for an hour. 2.6 g (13.4 mmol) of *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC) was added and stirred for another hour. A solution of 2.3 g (13.4 mmol) *p*-aminomethylstyrene · HCl (**8**) and 2 mL (13.4 mmol) of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) in 20 mL of dry methylene chloride was prepared and dropped to the latter solution at 0 °C. The mixture was stirred for 20 h at 25 °C, then washed with water (3 × 50 mL), and dried with magnesium sulfate.

4-Vinyl-{3,5-bis[3-(2-tetrahydropyranyloxy)propyloxy]benzoylaminomethyl}benzene (9a). *From G-1 Dendron Acid **6a***. Chromatographic separation (silica gel, hexane/ethyl acetate (3:1/v:v)) gave 4.9 g (80%) of **9a** as colorless crystals, mp 58−59 °C. ^{1}H NMR ($CDCl_3$): δ 1.3−1.8 (m, 12H, THP−CH_2), 2.0 (m, 4H, CH_2), 3.3−3.5 (m, 4H, OCH_2), 3.7−3.9 (m, 4H, OCH_2), 4.0 (t, 4H, ArOCH_2), 4.5 (t, 4H, THP−CH, NHCH_2), 5.2 (d, 1H, CH=CH_2), 5.7 (d, 1H, CH=CH_2), 6.5 (t, 1H, ArH), 6.6−6.7 (dd, 1H, CH=CH_2), 6.9 (d, 3H, ArH, NH), 7.2 (d, 2H, ArH), 7.3 (d, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ 19.5, 25.3 (THP−CH_2), 29.5 (CH_2), 30.6 (THP−CH_2), 43.7 ($NHCH_2$), 62.2 (OCH_2), 63.8 (THPOCH_2), 65.1 (ArOCH_2), 98.8 (THP−CH), 104.4, 105.5 (Ar), 113.8 (CH=CH_2), 126.4, 127.9, 136.3, 136.4, 136.7 (Ar), 137.8 (CH=CH_2), 160.1 (OAr), 167.2 (CONH). MS (70 eV); *m*/*z* (%): 553 (10) [M^+], 385 (100) [M^+ − 2THP]. Calcd for $C_{32}H_{43}NO_7$ (553.7): C, 69.41; H, 7.83; N, 2.52. Found: C, 69.09; H, 7.63; N, 2.69.

4-Vinyl-{3,5-bis{3-[3,5-bis[3-(2-tetrahydropyranyloxy)propyloxy]benzoylamino]propyloxy}benzoylaminomethyl}benzene (10a). *From G-2 Dendron Acid **7a***. Chromatographic separation (silica gel, hexane/ethyl acetate (1:2/v:v)) gave 3.7 g (85%) of **10a** as colorless crystals, mp 56−58 °C. ^{1}H NMR ($CDCl_3$): δ 1.4−1.9 (m, 24H, THP−CH_2), 1.9−2.1 (m, 12H, CH_2), 3.4−3.6 (m, 12H, OCH_2, NHCH_2), 3.7−3.8 (m, 8H, OCH_2), 3.9 (t, 4H, ArOCH_2), 4.0−4.1 (t, 8H, ArOCH_2), 4.5 (m, 6H, THP−CH, NHCH_2), 5.2 (d, 1H, CH=CH_2), 5.7 (d, 1H, CH=CH_2), 6.4 (t, 1H, ArH), 6.5 (t, 2H, ArH), 6.6−6.7 (dd, 1H, CH=CH_2), 6.8 (d, 2H, ArH), 6.9 (d, 4H, ArH), 7.0 (t, 2H, NH), 7.2 (t, 1H, NH), 7.3 (d, 2H, ArH), 7.4 (d, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ 19.5, 25.3 (THP−CH_2), 28.9, 29.5 (CH_2), 30.6 (THP−CH_2), 37.5, 43.7 ($NHCH_2$), 62.3 (OCH_2), 63.8 (THPOCH_2), 65.2, 66.1 (ArOCH_2), 98.9 (THP−CH), 104.4, 105.5, 105.6, 106.7 (Ar), 113.7 (CH=CH_2), 126.3, 127.9 136.3, 136.4, 136.5, 136.6 (Ar), 137.9 (CH=CH_2), 159.7, 160.1 (OAr), 167.0, 167.5 (CONH). FAB−MS *m*/*z* (%): 1246 (1) [M^+ + Na], 1125 (0.7) [M^+ + H]. Calcd for $C_{68}H_{93}N_3O_{17}$ (1224.5): C, 66.70; H, 7.65; N, 3.43. Found: C, 66.33; H, 7.41; N, 3.23.

4-Vinyl-{3,5-bis{3-[2-(trimethylsilyl)ethoxycarbonylamino]propyloxy}benzoylaminomethyl}benzene (9b). *From G-1 Dendron Acid **6c***. Chromatographic separation (silica gel, hexane/ethyl acetate (2:1/v:v)) gave 4,6 g (76%) of **9b** as colorless crystals, mp 79−81 °C. ^{1}H NMR ($CDCl_3$): δ −0.1 (s, 18H, TMS), 0.9 (t, 4H, TMSCH_2), 1.9 (m, 4H, CH_2), 3.2 (m, 4H, NHCH_2), 3.9 (t, 4H, ArOCH_2), 4.0 (t, 4H, OCH_2), 4.5 (d, 2H, CH_2), 5.2 (m, 3H, CH=CH_2, NH), 5.7 (d, 1H, CH=CH_2), 6.4 (t, 1H, ArH), 6.6−6.7 (dd, 1H, CH=CH_2), 6.9 (d, 3H, ArH, NH), 7.2 (d, 2H, ArH), 7.3 (d, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ −1.6 (TMS), 17.6 (TMSCH_2), 29.2 (CH_2), 37.9, 43.6 ($NHCH_2$), 62.8, 65.6 (OCH_2), 104.3, 105.5 (Ar), 113.7 (CH=CH_2), 126.2, 127.9, 136.2, 136.3, 136.5 (Ar), 137.8 (CH=CH_2), 156.8 (NHCOO), 159.7 (OAr), 167.0 (CONH). MS (70 eV) *m*/*z* (%): 671 (3) (HRMS: calcd, 671.342208; found, 671.34466) [M^+]. Calcd for $C_{34}H_{53}N_3O_7Si_2$ (671.9): C, 60.77; H, 7.95; N, 6.25. Found: C, 60.63; H, 7.58; N, 6.09.

4-Vinyl-{3,5-bis{3-{3,5-bis[3-[2-(trimethylsilyl)ethoxycarbonylamino]propyloxy]benzoylamino}propyloxy}benzoylaminomethyl}benzene (10b). *From G-2 Dendron Acid **7c***. Chromatographic separation (silica gel, hexane/ethyl acetate (1:2/v:v)) gave 6.7 g (65%) of **10b** as colorless crystals, mp 68−71 °C. ^{1}H NMR ($CDCl_3$): δ −0.1 (s, 36H, TMS), 0.9 (t, 8H, TMSCH_2), 1.8 (m, 8H, CH_2), 1.9 (m, 4H, CH_2), 3.2 (m, 8H, NHCH_2), 3.5 (m, 4H, NHCH_2), 3.9 (m, 12H, ArOCH_2), 4.1 (t, 8H, OCH_2), 4.5 (d, 2H, CH_2), 5.2 (m, 5H, CH=CH_2, NH), 5.7 (d, 1H, CH=CH_2), 6.3 (t, 1H, ArH), 6.4 (t, 2H, ArH), 6.6−6.7 (dd, 1H, CH=CH_2), 6.8 (d, 2H, ArH), 6.9 (d, 4H, ArH), 7.2 (d, 2H, ArH), 7.3 (m, 4H, ArH, NH), 7.4 (t, 1H, NH). ^{13}C NMR ($CDCl_3$): δ −1.6 (TMS), 17.7 (TMSCH_2), 28.8, 29.4 (CH_2), 37.4, 37.9, 43.7 ($NHCH_2$), 62.8, 65.7, 65.9 (OCH_2), 104.4, 105.5, 105.6 (Ar), 113.8 (CH=CH_2), 126.3, 128.1, 136.2, 136.3, 136.5, 136.6 (Ar), 138.0 (CH=CH_2), 156.9 (NHCOO), 159.6, 159.8 (OAr), 167.0, 167.4 (CONH). FAB; *m*/*z* (%): 1484 (0.2) [M^+ + Na], 1461 (0.1) [M^+]. Calcd for $C_{72}H_{113}N_7O_{17}Si_4$ (1461.1): C, 59.19; H, 7.80; N, 6.71. Found: C, 59.04; H, 7.58; N, 6.38.

General Polymerization Procedure. Then 0.82 mmol of the monomer, 0.4 mL (3 mol %) of a 0.06 M initiator solution in toluene, and 0.6 mL of toluene were stirred under nitrogen in a sealed tube at the polymerization temperature for 72 h. The polymer was dissolved in THF, precipitated with methanol/water (4:1/v:v), and lyophilized. For details see Table 2.

Poly{4-vinyl-{3,5-bis[3-(2-tetrahydropyranyloxy)-propyloxy]benzoylaminomethyl}benzene} (11a). *From G-1 Monomer **9a***. ^{1}H NMR ($CDCl_3$): δ 1.2−1.8 (br, 15H, THP−CH_2, CH, CH_2), 2.0 (br, 4H, CH_2), 3.3−3.4 (br, 4H, OCH_2), 3.7−3.8 (br, 4H, OCH_2), 4.0 (br, 4H, ArOCH_2), 4.2−4.5 (br, 4H, THP−CH, NHCH_2), 6.1−6.6 (br, 3H, ArH), 6.7−7.1 (br, 4H, ArH), 7.7−8.3 (br, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 19.4, 25.2 (THP−CH_2), 29.4 (CH_2), 30.5 (THP−CH_2), 39.5 (CH_2), 43.0 ($NHCH_2$), 43.4 (CH), 62.1 (OCH_2), 63.7 (THPOCH_2), 64.8 (ArOCH_2), 98.7 (THP−CH), 104.3, 105.5 (Ar), 126.4, 127.4, 135.6, 136.3, 143.0 (Ar), 159.9 (OAr), 167.4 (CONH). TGA: 280 °C (−2THP). DSC: 27.3 °C (T_g). Calcd for $(C_{32}H_{43}NO_7)_n$ $(553.7)_n$: C, 69.41; H, 7.83; N, 2.52. Found: C, 68.58; H, 7.70; N, 2.12.

Poly{4-vinyl-{3,5-bis[3-[2-(trimethylsilyl)ethoxycarbonylamino]propyloxy]benzoylaminomethyl}benzene} (11b). *From G-1 Monomer* ***9b***. ^{1}H NMR ($CDCl_3$): δ −0.1 (br, 18H, TMS), 0.9 (br, 7H, TMSCH_2, CH_2, CH), 1.5−1.9 (br, 4H, CH_2), 3.0−3.2 (br, 4H, NHCH_2), 3.5−3.8 (br, 4H, ArOCH_2), 3.9−4.0 (br, 4H, OCH_2), 4.0−4.5 (br, 2H, CH_2), 6.0−6.4 (br, 1H, ArH), 6.4−6.6 (br, 3H, ArH), 6.8−7.2 (br, 4H, ArH). ^{13}C NMR ($CDCl_3$): δ −1.0 (TMS), 18.7 (TMSCH_2), 30.7 (CH_2), 38.8, 44.3 (NHCH_2), 63.7, 66.7 (OCH_2), 107.1 (br, Ar), 128.7, 137.5 (br, Ar), 159.1 (OAr), 161.5 (NHCOO), 169.3 (CONH). TGA: 156 °C (−TEOC). DSC: 52.3 °C (T_g). Calcd for $(C_{34}H_{53}N_3O_7Si_2)_n$ (671.9)$_n$: C, 60.77; H, 7.95; N, 6.25. Found: C, 60.28; H, 7.84; N, 5.71.

Poly{4-vinyl-{3,5-bis{3-[3,5-bis[3-(2-tetrahydropyranyloxy)propyloxy]benzoylamino]propyloxy}benzoylaminomethyl}benzene} (12a). *From G-2 Monomer* ***10a***. ^{1}H NMR ($CDCl_3$): δ 1.2−1.8 (br, 27H, THP−CH_2, CH, CH_2), 1.9−2.1 (br, 12H, CH_2), 3.3−3.5 (br, 12H, OCH_2, NHCH_2), 3.7−4.1 (br, 20H, OCH_2, ArOCH_2), 4.5 (br, 6H, THP−CH, NHCH_2), 6.1−6.5 (br, 3H, ArH), 6.6−7.0 (br, 8H, ArH), 7.6−8.3 (br, 3H, NH). ^{13}C NMR ($CDCl_3$): δ 19.5, 25.3 (THP−CH_2), 29.4, 29.5 (CH_2), 30.6 (THP−CH_2), 37.2, 43.2 (NHCH_2), 62.2 (OCH_2), 63.8 (THPOCH_2), 65.0, 65.1 (ArOCH_2), 98.8 (THP−CH), 104.3, 105.6 (Ar), 126.3, 127.9 128.2, 128.6, 136.4 (Ar), 159.9 (OAr), 167.6 (CONH). TGA: 285 °C (−4THP). DSC: 41.5 °C (T_g). Calcd for $(C_{68}H_{93}N_3O_{17})_n$ (1224.5)$_n$: C, 66.70; H, 7.65; N, 3.43. Found: C, 66.18; H, 7.41; N, 3.16.

Poly{4-vinyl-{3,5-bis{3-{3,5-bis[3-[2-(trimethylsilyl)-ethoxycarbonylamino]propyloxy]benzoylamino}-propyloxy}benzoylaminomethyl}benzene} (12b). *From G-2 Monomer* ***10b***. ^{1}H NMR ($CDCl_3$): δ −0.1 (br, 36H, TMS), 0.9 (br, 11H, TMSCH_2, CH_2, CH), 1.6−2.1 (br, 12H, CH_2), 3.1−3.2 (br, 8H, NHCH_2), 3.3−3.5 (br, 4H, NHCH_2), 3.5−4.0 (br, 12H, ArOCH_2), 4.0−4.2 (br, 8H, OCH_2), 4.2−4.5 (br, 2H, CH_2), 6.2−6.6 (br, 5H, ArH), 6.7−7.1 (br, 8H, ArH). ^{13}C NMR ($CDCl_3$): δ −1.2 (TMS), 18.7 (TMSCH_2), 30.3, 30.7 (CH_2), 38.4, 38.8, 39.2 (NHCH_2), 63.7, 64.3, 66.7 (OCH_2), 105.5, 107.0 (Ar), 125.3, 137.5 (br, Ar), 159.0 (OAr), 161.4 (NHCOO), 169.4 (CONH). TGA: 260 °C (−4TEOC). Calcd for $(C_{72}H_{113}N_7O_{17}Si_4)_n$ (1461.1)$_n$: C, 59.19; H, 7.80; N, 6.71. Found: C, 58.61; H, 7.51; N, 6.32.

General Procedure for Preparation of Hydroxy Polymers. A solution of 2% hydrochloric acid in methanol (5 mL) was dropped into a solution of 0.2 g of the protected hydroxy polymer in 30 mL of THF and stirred for 5 h. The polymer was precipitated with an aqueous sodium chloride solution. The polymer was dissolved in 30 mL of DMF and stirred with 20 mL of a solution of 2% hydrochloric acid in methanol for 20 h. The polymer was precipitated with an aqueous sodium chloride solution and dried in vacuo.

Poly{4-vinyl-[3,5-bis(3-hydroxypropyloxy)benzoylaminomethyl]benzene} (11c). *From the THP Protected Polymer* ***11a***. ^{1}H NMR ([D_7] DMF): δ 1.2−1.7 (br, 3H, CH, CH_2), 1.8−2.0 (br, 4H, CH_2), 3.6−3.7 (br, 4H, OCH_2), 4.3−4.6 (br, 2H, NHCH_2), 4.8 (br, 2H, OH), 6.2−6.6 (br, 3H, ArH), 6.8−7.2 (br, 4H, ArH), 8.8−9.3 (br, 1H, NH). ^{13}C NMR ([D_7] DMF): δ 33.1 (CH_2), 40.4 (CH_2), 43.3 (NHCH_2), 44.4 (CH), 58.5 (OCH_2), 65.6 (ArOCH_2), 104.6, 106.3 (Ar), 127.9, 137.4, 144.4 (br, Ar), 160.8 (OAr), 167.1 (CONH). TGA: 330 °C. DSC: 60.3 °C (T_g). $(C_{12}H_{27}NO_5)_n$ (265.3)$_n$.

Poly{4-vinyl-{3,5-bis[3-[3,5-bis(3-hydroxypropyloxy)-benzoylamino]propyloxy]benzoylaminomethyl}-benzene} (12c). *From THP-Protected Polymer* ***12a***. ^{1}H NMR ([D_7] DMF): δ 1.1−1.8 (br, 3H, CH, CH_2), 1.8−1.9 (br, 8H, CH_2), 1.9−2.1 (br, 4H, CH_2), 3.3−3.5 (br, 4H, NHCH_2), 3.7 (br, 8H, HOCH_2), 3.9−4.2 (br, 12H, ArOCH_2), 4.7 (br, 4H, OH), 4.36−4.6 (br, 2H, NHCH_2), 6.2−6.5 (br, 5H, ArH), 6.8−7.2 (br, 8H, ArH), 8.5−8.7, 8.7−9.2 (br, 3H, NH). ^{13}C NMR ([D_7] DMF): δ 25.9, 33.2 (CH_2), 37.5, 49.5 (NHCH_2), 58.6 (HOCH_2), 65.6, 66.5 (ArOCH_2), 104.5, 105.5, 106.3 (Ar), 128.2, 137.4 (Ar), 160.7 (OAr), 167.3 (CONH). TGA: 300 °C (−OH−G−1). DSC: 77.5 °C (T_g). $(C_{48}H_{61}N_3O_{13})_n$ (888.0)$_n$.

General Procedure for the Preparation of Amino Polymers. Then 0.2 g of the protected amino polymer and 20 mL of trifluoroacetic acid were stirred for 20 h at room temperature. The trifluoroacetic acid was removed and the residue was lyophilized from water.

Poly{4-vinyl-[3,5-bis(3-aminopropyloxy)benzoylaminomethyl]benzene} 2 · Trifluoroacetic Acid (11d). *From TEOC-Protected Polymer* ***11b***. ^{1}H NMR ([D_4] MeOH): δ 0.9−1.8 (br, 3H, CH_2, CH), 1.9−2.2 (br, 4H, CH_2), 2.9−3.2 (br, 4H, NH_3CH$_2$), 3.8−4.1 (br, 4H, ArOCH_2), 4.1−4.5 (br, 2H, OCH_2), 6.0−6.4 (br, 3H, ArH, NH), 6.4−6.6 (br, 1H, ArH), 6.6−7.1 (br, 4H, ArH). ^{13}C NMR ([D_4] MeOH): δ 28.2 (CH_2), 38.4, 44.2 (NHCH_2), 66.4 (OCH_2), 105.1, 107.2 (Ar), 118.4 (q, CF_3), 128.7, 137.5 (br, Ar), 161.2 (OAr), 162.5 (q, CF_3COO), 196.5 (CONH). TGA: 180 °C (−CF_3COOH). DSC: 119 °C (T_g). Calcd for $(C_{26}H_{31}N_3O_7F_6)_n$ (611.5)$_n$: C, 51.06; H, 5.11; N, 6.87. Found: C, 51.76; H, 5.09; N, 6.79.

Poly{4-vinyl-{3,5-bis[3-[3,5-bis(3-aminopropyloxy)-benzoylamino]propyloxy]benzoylaminomethyl}benzene} 4 · Trifluoroacetic acid (12d). *From TEOC-Protected Polymer* ***12b***. ^{1}H NMR ([D_4] MeOH): δ 1.7−2.0 (br, 4H, CH_2), 2.0−2.2 (br, 8H, CH_2), 2.9−3.2 (br, 8H, NH_3CH$_2$), 3.3−3.5 (br, 4H, NHCH_2), 3.7−4.2 (br, 12H, ArOCH_2), 4.2−4.5 (br, 2H, CH_2), 6.3−6.6 (br, 5H, ArH), 6.7−7.1 (br, 8H, ArH). ^{13}C NMR ([D_4] MeOH): δ 28.2, 30.2 (CH_2), 38.4, 38.5, 44.3 (NHCH_2), 66.4, 68.1 (OCH_2), 105.6, 107.1 (Ar), 118.2 (q, CF_3), 128.3, 137.6 (br, Ar), 161.1, 161.5 (OAr), 163.0 (q, CF_3COO), 169.5 (CONH). TGA: 103 °C (−CF_3COOH), 181 °C (−$(NH_2)_2$G-1, CF_3COOH). DSC: 127 °C (T_g). Calcd for $(C_{56}H_{69}N_7O_{17}F_{12})_n$ (1340.1)$_n$: C, 50.18; H, 5.19; N, 7.32. Found: C, 50.13; H, 4.93; N, 6.88.

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