The synthesis and polymerization of a hyperbranched polyether macromonomer

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A novel class of macromonomer, in which the macromolecular part is a hyperbranched dendritic polyether prepared by the 'convergent-growth' approach, is synthesized and characterized. Free-radical copolymerization with styrene at various feed ratios gives a series of unique copolymers.

(Keywords: polyether macromonomer; dendrite; synthesis)

INTRODUCTION

The synthesis of polymers with controlled molecular architecture has increased in importance due to the rising demands for new speciality polymers possessing novel properties[1]. One of the major methods for controlling molecular architecture is by controlling the number and location of branches through the formation of graft and star polymers and polymerization of macromonomers. The synthesis of copolymers from macromonomers is a major field of study and has received increased recognition during the last decade[2–5].

Recently, we reported[6–9] a new 'convergent-growth' approach to dendritic macromolecules with branches at each monomer unit. This approach is characterized by reactions occurring at a single functional group at the 'focal' point of the growing dendritic macromolecule. The presence of a single functional group at the focal point increases the ease of purification and the degree of control over the architecture of the final dendritic macromolecule. It also gives a well defined functionality to which other reactive molecules can be attached. If this reactive molecule contains a polymerizable group we can envisage the production of a unique class of macromonomer in which the macromolecular part is a hyperbranched dendritic moiety. This type of chemistry is not available to dendritic macromolecules produced by the divergent or 'Starburst' methodology[10–17].

For this purpose, we investigated the synthesis of a series of dendritic macromonomers based on the polyether macromolecules prepared previously[6–9]. It was also expected that a study of the copolymerization of macromonomers of various sizes and steric requirements with varying molar percentages of styrene would provide insight into the degree of steric congestion around the focal point.

EXPERIMENTAL

General directions

The hydroxymethyl-terminated dendritic polyether macromolecules were prepared and purified as described previously[6–9]. 4-Chloromethyl styrene (Eastman Kodak) was used as supplied. THF was purified by distillation in the presence of the sodium salt of benzophenone. Styrene was distilled at reduced pressure prior to use and toluene was purified and degassed by distillation from sodium under an argon atmosphere. Infra-red spectra were recorded on a Nicolet IR/44 spectrophotometer as thin films or KBr discs. ^{1}H n.m.r. spectra were recorded on solutions in $CDCl_3$ on a Bruker WM 300 (300 MHz) spectrometer using the solvent proton signal as standard. ^{13}C n.m.r. spectra were recorded at 75 MHz on a Bruker WM300 spectrometer using $CDCl_3$ as the solvent and the solvent carbon signal as internal standard. Mass spectra were obtained on a Kratos MS890 using either e.i. or f.a.b. ionization, the latter being run with 3-nitrobenzyl alcohol as the matrix. Analytical t.l.c. was performed on commercial Merck plates coated with silica gel FF_{254} (0.25 mm thick). Silica for flash chromatography was Merck Kieselgel 60 (230–400 Mesh). Size exclusion chromatography (s.e.c.) was carried out on a Nicolet LC/9560 Chromatograph connected to a Milton Roy refractoMonitor IV refractive-index detector and data analysis was performed by an IBM system 9000 computer. Five 10 μm IBM GPC/SEC columns (300 × 7.7 mm) connected in series in order of decreasing pore size were used with THF as solvent. Molecular weight data are reported relative to a polystyrene calibration. Elemental analyses were made by MHW Laboratories, Phoenix, Arizona.

General procedure for the synthesis of the macromonomers

To a solution of the benzylic alcohol (1.00 equivs.) in freshly distilled dry THF was added sodium hydride (60% dispersion in oil) (1.30 equivs.) and the reaction mixture stirred at room temperature under nitrogen for 30 minutes. 4-Chloromethyl styrene **1** (5.0 equivs.) in dry THF was added and the mixture heated at reflux for 18 h. The reaction mixture was cooled, carefully hydrolysed, and evaporated to dryness. The residue was partitioned between water and CH_2Cl_2 and the aqueous layer extracted with CH_2Cl_2 (3×). The organic layers were then dried (Mg_2SO_4) and evaporated to dryness under reduced pressure. The crude product was purified as outlined below.

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4-Benzyloxymethylstyrene **9**. This was prepared as described in the general procedure above from benzyl alcohol **6** and purified by flash chromatography eluting with 1:1 hexane/CH_2Cl_2, gradually increasing to CH_2Cl_2 to give **9** as a colourless oil: yield 76%; (Found: **C**, 85.34; **H**, 6.99. $C_{16}H_{16}O$ requires **C**, 85.68; **H**, 7.19%). I.r. 1600, 1430, 1365, 1160 and 1070 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 4.58 (s, 4H, CH_2OAr), 5.26 and 5.29 (d of d, 1H, J = 1 and 8 Hz, =**CH**), 5.76 and 5.82 (d of d, 1H, J = 1 and 18 Hz, =**CH**), 6.72 and 6.78 (d of d, 1H, J = 8 and 18 Hz, =**CH**) and 7.29–7.45 (m, 9H, Ph**H**); mass spectrum, m/z (e.i.) 224.

[*G-3*]-*styrene* **7**. This was prepared from [G-3]-OH **4** and purified by flash chromatography eluting with 2:3 hexane/CH_2Cl_2 gradually increasing to CH_2Cl_2 to give **7** as a colourless glass: yield 77%; (Found: **C**, 79.98; **H**, 6.03. $C_{114}H_{100}O_{15}$ requires **C**, 80.07; **H**, 5.89%). I.r. 1600, 1430, 1365, 1160 and 1070 cm^{-1}, ^1H n.m.r. ($CDCl_3$) δ 4.46 and 4.49 (each s, 4H, CH_2OCH_2), 4.94 and 4.97 (each s, 12H, Ar-CH_2O), 5.00 (s, 16H, Ph-CH_2O), 5.19 and 5.22 (d of d, 1H, J = 1 and 8 Hz, =**CH**), 5.68 and 5.74 (d of d, 1H, J = 1 and 18 Hz, =**CH**), 6.53–6.72 (m, 22H, =**CH** and Ar**H**) and 7.27–7.41 (m, 44H, Ar'**H** and Ph**H**); ^{13}C n.m.r. ($CDCl_3$) δ 69.93, 70.10 (CH_2O), 71.65, 71.76 (CH_2OCH_2), 101.17, 101.42, 106.23, 106.46 (Ar **C**), 113.69, 126.14 (Ar'**C**), 127.42, 127.85, 128.42 (Ph **C**H), 136.38, 136.62, 137.65, 139.08, 139.22, 140.70, 159.83, 159.92 and 159.99 (Ar, Ar' and Ph **C**); mass spectrum, m/z (f.a.b.) 1708/1709 (*ca.* 1:1).

[*G-4*]-*styrene* **3**. This was prepared from [G-4]-OH **2** and purified by flash chromatography eluting with 1:3 hexane/CH_2Cl_2 gradually increasing to CH_2Cl_2 to give **3** as a colourless glass: yield 73%; (Found: **C**, 79.58; **H**, 5.95. $C_{226}H_{196}O_{31}$ requires **C**, 79.65; **H**, 5.80%). I.r. 1600, 1435, 1365, 1170 and 1075 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 4.44 and 4.47 (each s, 4H, CH_2OCH_2), 4.91 (s, 28H, Ar-CH_2O), 4.99 (s, 32H, Ph-CH_2O), 5.16 and 5.20 (d of d, 1H, J = 1 and 8 Hz, =**CH**), 5.66 and 5.72 (d of d, 1H, J = 1 and 18 Hz, =**CH**), 6.51–6.66 (m, 46H, Ar**H** and =**CH**) and 7.26–7.40 (m, 84H, Ar'**H** and Ph**H**); ^{13}C n.m.r. ($CDCl_3$) δ 69.71, 69.79 (CH_2O), 71.60, 71.71 (CH_2OCH_2), 101.10, 101.39, 106.19, 106.41 (Ar **C**), 113.64, 126.08 (Ar'**C**), 127.35, 127.77, 128.36 (Ph **C**H), 136.33, 136.61, 136.74, 137.65, 139.08, 139.27, 140.68, 159.79, 159.86 and 159.94 (Ar, Ar' and Ph **C**).

[*G-5*]-*styrene* **8**. This was prepared from [G-5]-OH **5** and purified by flash chromatography eluting with 1:3 hexane/CH_2Cl_2 gradually increasing to CH_2Cl_2 to give **8** as a colourless glass: yield 67%; (Found: **C**, 79.35; **H**, 6.00. $C_{450}H_{388}O_{63}$ requires **C**, 79.44; **H**, 5.75%). I.r. 1600, 1435, 1365, 1170 and 1075 cm^{-1}, ^1H n.m.r. ($CDCl_3$) δ 4.47 and 4.50 (each s, 4H, CH_2OCH_2), 4.96 (s, 60H, Ar-CH_2O), 5.02 (s, 64H, Ph-CH_2O), 5.19 and 5.23 (d of d, 1H, J = 1 and 8 Hz, =**CH**), 5.74 and 5.79 (d of d, 1H, J = 1 and 18 Hz, =**CH**), 6.55–6.76 (m, 94H, Ar**H** and =**CH**) and 7.26–7.43 (m, 164H, Ar'**H** and Ph**H**); ^{13}C n.m.r. ($CDCl_3$) δ 69.75, 69.84 (CH_2O), 71.63, 71.73 (CH_2OCH_2), (peak too small to observe), 101.42, 106.00, 106.23 (Ar **C**), 113.68, 126.12 (Ar'**C**), 127.41, 127.82, 128.41 (Ph **C**H), 136.37, 136.65, 136.78, 137.68, 139.12, 139.32, 140.71, 159.79, 159.90 and 159.98 (Ar, Ar' and Ph **C**).

Copolymerization of the macromonomers with polystyrene

All the copolymerizations were carried out as described below for a 1:4 mixture (by weight) of [G-3]-styrene with styrene. To the third generation macromonomer **7** (600 mg, 0.35 mmol) was added freshly distilled styrene (2.40 g, 23.1 mmol), AIBN (40 mg, 0.24 mmol, 1.0 mol%), freshly distilled and degassed toluene (2.50 g) and the solution heated at 70–75°C under argon for 26 h. The reaction mixture was then precipitated into hexane, the precipitated solid collected and reprecipitated into 1:3 isopropanol/acetone. The purified product was then reprecipitated into methanol and the white solid collected by filtration: yield 64%; i.r. 3030, 2950, 1600, 1495, 1460, 1165 and 700 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 1.25–2.10 (br m, backbone CH_2 and CH), 4.42 (br s, CH_2OCH_2), 4.93 (br s, Ar-CH_2), 5.00 (br s, Ph-CH_2), 6.25–7.20 (br m, Ar**H** and styrene Ar**H**) and 7.26–7.55 (m, Ph**H**); ^{13}C n.m.r. ($CDCl_3$) δ 40–47 (broad series of peaks, backbone CH_2 and CH), 69.95, 70.40 (Ar and Ph-CH_2O), 71.81, 71.92 (CH_2OCH_2), 101.09, 101.55, 106.34, 106.46 (Ar**C**), 125.46, 125.61, 127.52, 127.96, 128.54 (aromatic **C**), 136.72, 139.16, 140.96 (Ar**C**), 144.5–146.5 (br, aromatic **C**), 160.00 and 160.11 (Ar **C**).

All other copolymerizations were carried out using a similar procedure; feed ratios, yields and molecular weight data (polystyrene standards) are outlined in *Table 1*.

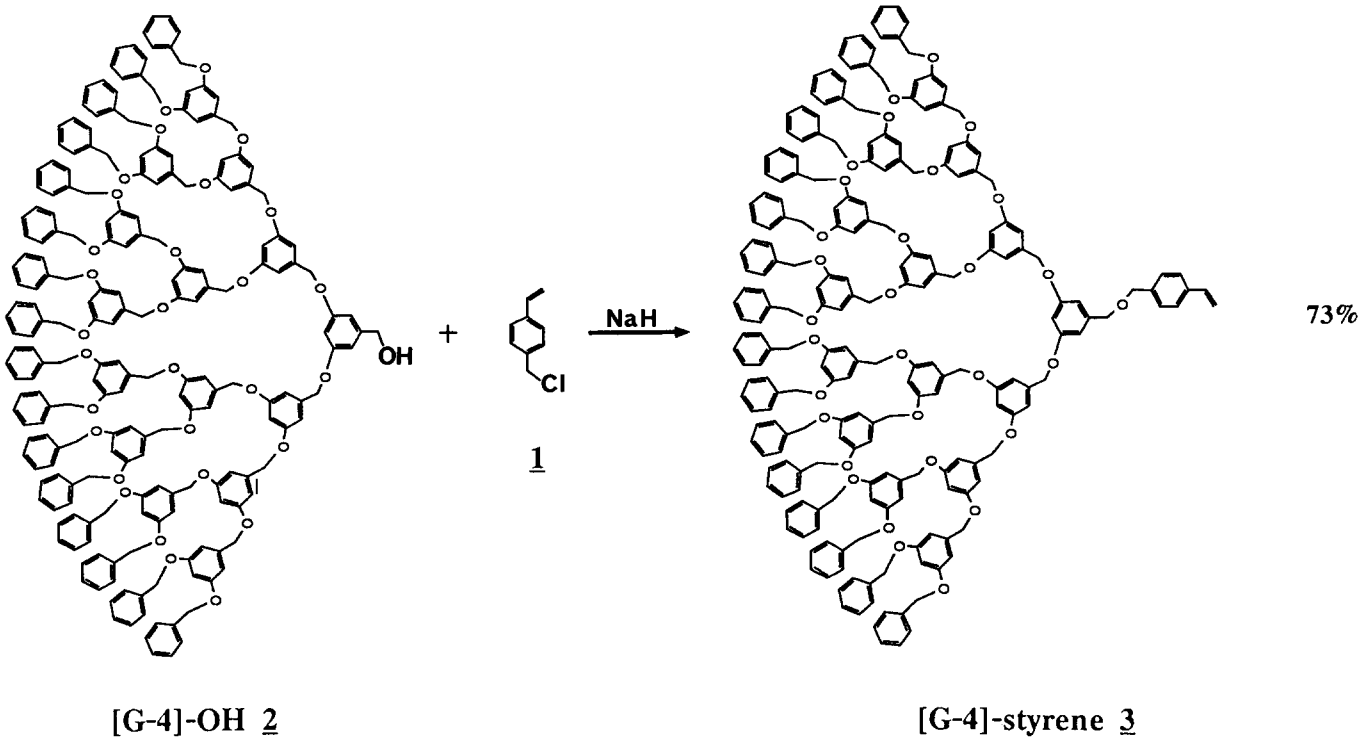
RESULTS AND DISCUSSION

Synthesis

As described previously[6–9], a fundamental aspect of the convergent approach to dendritic macromolecules is the presence of a single functional group at the focal point of the macromolecule. By analogy with the synthesis of other macromonomers[2–5] a molecule containing a polymerizable group can be attached to this single functional group. In our case, due to synthetic ease, it was decided to utilize the nucleophilic properties of the anion generated from the focal-point hydroxymethyl group in the displacement of chloride ion from commercially available 4-chloromethyl styrene, **1**. This is illustrated in *Scheme 1* for the fourth generation alcohol, [G-4]-OH, **2**, which gives the corresponding dibenzyl ether, [G-4]-styrene, **3**. Products could be easily purified by flash chromatography due to the large R_f differences between the starting alcohol and the desired ether product. The reaction was also carried out with the corresponding third, [G-3]-OH, **4**, and fifth generation alcohols, [G-5]-OH, **5**. A sterically non-demanding model compound, 4-Benzyloxymethylstyrene **9**, was similarly prepared from **1**, and benzyl alcohol, **6**. Yields of purified products were 77% for [G-3]-styrene, **7**, decreasing to 67% for [G-5]-styrene **8**. The different generation macromonomers prepared correspond to nominal molecular weights (calculated on the basis that C = 12.01, H = 1.008, O = 16.00) of 1710, 3408 and 6804 for G = 3, 4 and 5, respectively. Confirmation of the molecular weights were by s.e.c. with comparison to known calibrated dendritic polyether samples[6–9] and to the starting materials, also the molecular ion of the third generation macromonomer, **7**, can be observed by f.a.b. mass spectrometry. The introduction of the styrene unit at the focal point of the dendrimers was easily confirmed by ^1H and ^{13}C n.m.r. spectroscopy. *Figure 1* shows the

Table 1 Copolymers of dendritic macromonomers with styrene

Entry	Macromonomer		Macromonomer (wt%)		Yield (%)	Copolymer	
	Generation	Structure	Feed	Product		M_w ($\times 10^3$)	M_n ($\times 10^3$)
1	[G-3]	**7**	1.0	1.0	76	42	28
2	[G-3]	**7**	3.0	3.2	72	44	31
3	[G-4]	**3**	3.0	3.1	69	40	27
4	[G-5]	**8**	3.0	2.9	68	45	34
5	[G-0]	**9**	20.0	19.2	81	40	21
6	[G-3]	**7**	20.0	21.0	64	49	35
7	[G-4]	**3**	20.0	20.7	62	53	37
8	[G-5]	**8**	20.0	19.6	61	50	34
9	[G-3]	**7**	30.0	31.3	59	71	46
10	[G-3]	**7**	40.0	41.3	52	79	48



Scheme 1

300 MHz ^{1}H n.m.r. spectrum of the fourth generation alcohol, **2**, and the corresponding macromonomer, **3**. The presence of the styrene unit is confirmed by the two sets of resonances at 5.18 and 5.69 ppm for the CH_2 of the vinyl group, also the resonance for the hydroxymethyl group at 4.51 ppm has disappeared and is replaced by two singlets for the dibenzyl ether group at 4.44 and 4.47 ppm. Integration of these resonances and comparison with the other resonances for the macromonomer **3** confirms both the structure and the generation number of the macromonomer **3**. Similarly, comparison of the ^{13}C n.m.r. spectra for **2** and **3** reveals the absence of the resonance for the CH_2OH at 65.4 ppm and the appearance of resonances at 71.6 and 71.7 ppm for the dibenzyl ether group; resonances in the aromatic/olefin region for the vinyl-benzene group are also present (*Figure 2*).

Copolymerization with styrene

Several novel copolymers were prepared by copolymerization of the macromonomers with styrene under standard free-radical conditions in 50% dry, degassed toluene using AIBN as initiator and heating to 70–75°C for 24 h (*Scheme 2*). The work-up and purification procedure were optimized to give copolymers of high purity and a summary of these polymerizations and characterization of the materials is given in *Table 1*. The decrease in yields for entries 9 and 10 is due to the need for repeated reprecipitations to obviate the difficulty in separating the copolymers containing a greater percentage of polyether dendrimers from unreacted macromonomer.

Figure 3 shows representative (entry 7 in *Table 1*) s.e.c. traces for both the macromonomer, **3**, and the purified copolymer, **10** (precipitated in isopropanol/acetone), which is free of unreacted macromonomer. The molecular

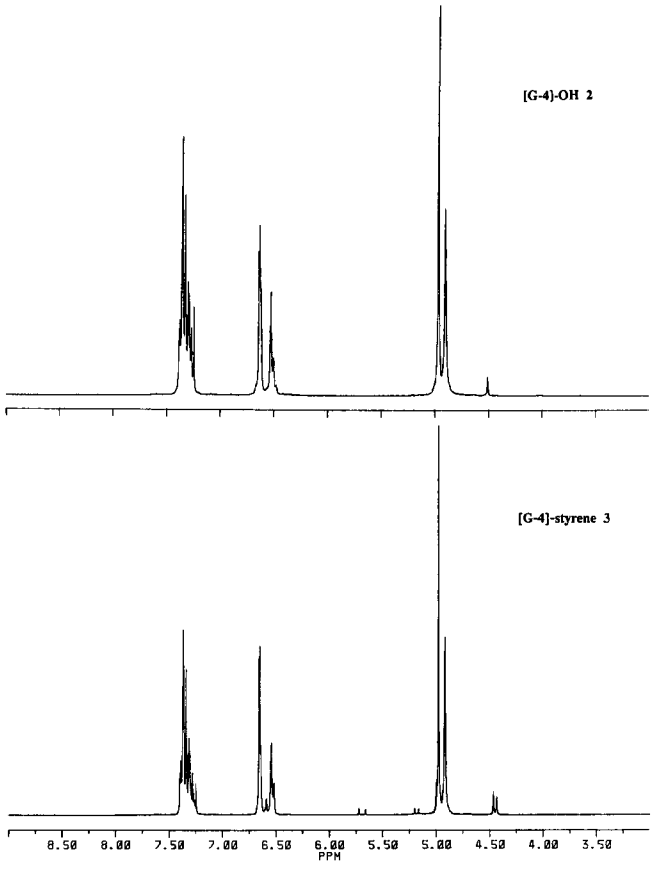


Figure 1 300 MHz ^{1}H n.m.r. spectra of [G-4]-OH and [G-4]-styrene, 3

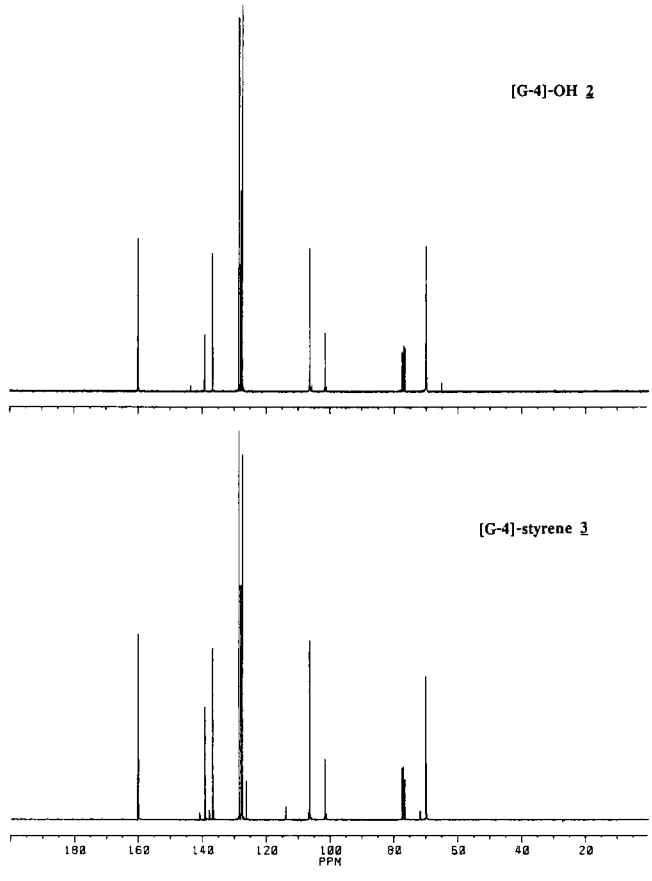
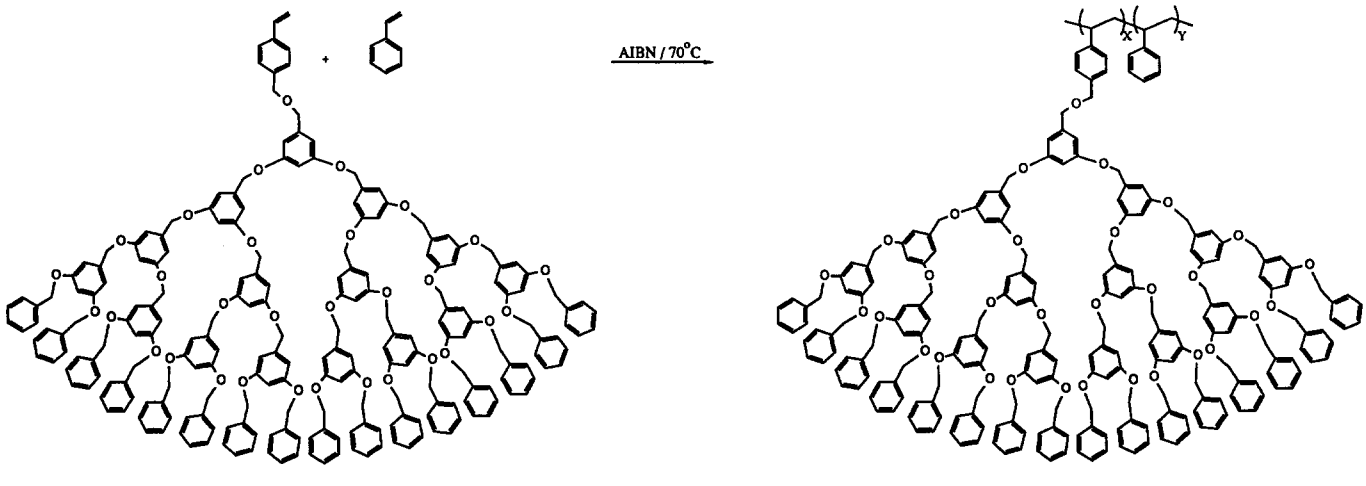


Figure 2 75 MHz ^{13}C n.m.r. spectra of [G-4]-OH, **2**, and [G-4]-styrene, **3**



[G-4]-styrene 3

Scheme 2

weights listed in *Table 1* are for purposes of comparison only since they are based on polystyrene calibrations (polystyrene standards were obtained from Polymer Laboratories, Amherst, MA). Dendritic macromolecules have been shown[6–9,18] to give much lower polystyrene-equivalent molecular weights in comparison with their absolute molecular weights. A complex relationship between absolute molecular weights and polystyrene-equivalent molecular weights for copolymers containing dendrimers of differing size and percentage incorporation would therefore be expected. As expected, *Table 1* shows that molecular weight increases with the percentage of the dendritic macromolecule in the feed.

The compositions of the purified copolymers were determined by ^{1}H n.m.r. spectroscopy. *Figure 4* shows the 300 MHz ^{1}H n.m.r. spectrum for the copolymer, **10**, containing the fourth generation macromonomer (entry 7 in *Table 1*, cf. *Figure 1*). Integration of the resonances

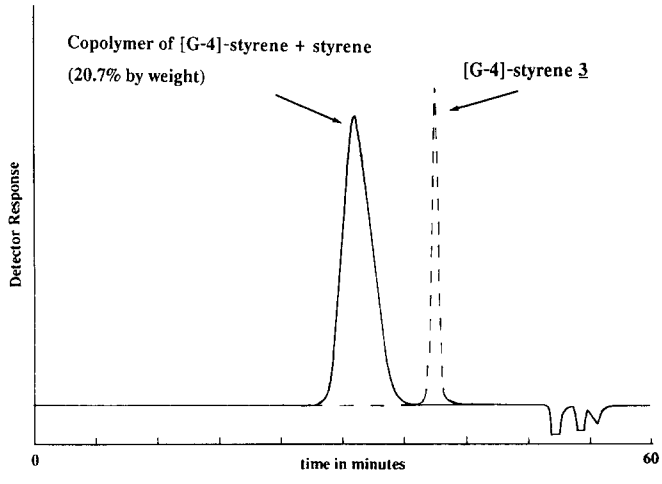


Figure 3 S.e.c. traces for [G-4]-styrene, **3**, and purified copolymer, **10**

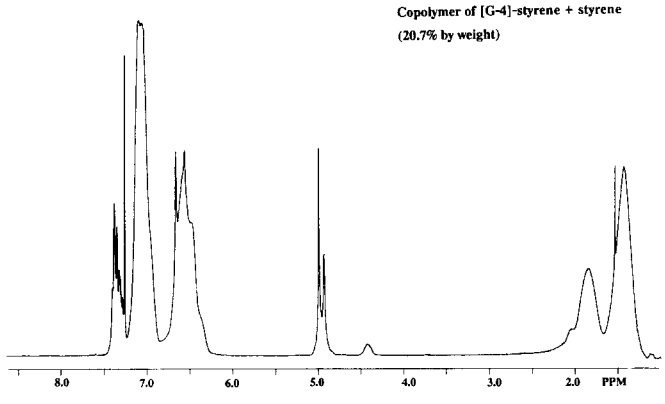


Figure 4 300 MHz ^{1}H n.m.r. spectrum of typical copolymer, **10**

for the Ar$\mathbf{CH}_2$O (*ca.* 5.0 ppm) groups of the dendrimer and comparison with the aromatic and aliphatic resonances yield relative styrene and dendrimer compositions. All of the experimental microanalyses found for these copolymers were found to be within the error for the theoretical values calculated from the compositions determined by ^{1}H n.m.r. spectroscopy.

Comparison of the feed ratios and product ratios for copolymers containing third generation macromonomer, **7** (entries 1, 2, 6, 9, 10), shows that on increasing the percentage of **7**, no apparent decrease in the incorporation of the macromonomer into the copolymer is observed. Also for entries 3, 4 and 7, 8 only a small decrease in incorporation is observed on going to the corresponding fourth generation, **3**, and fifth generation, **8**, macromonomers. When this is compared to entry 5 for the model monomer, benzyl 4-vinylbenzyl alcohol, **9**, no significant difference is observed. This suggests that steric crowding around the styrene unit covalently bound to the focal point of the dendrimer is not a major factor for the third and fourth generation macromonomers and is sufficient to decrease the relative incorporation for the fifth generation macromonomer only slightly. This is in agreement with our previous finding that it is only at generation five that decreases in yields for the synthesis of dendritic 'wedges' are observed.

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REFERENCES

1 Bikales, N. M. *Polymer* 1987, **19**, 11
2 Schulz, G. O. and Milkovich, R. *J. Appl. Polym. Sci.* 1982, **27**, 4773
3 Rempp, P. F. and Franta, E. *Adv. Polym. Sci.* 1984, **58**, 1
4 Tsukahara, Y., Mizuno, K., Segawa, A. and Yamashita, Y. *Macromolecules* 1989, **22**, 1546
5 Norton, R. L. and McCarthy, T. J. *Macromolecules* 1989, **22**, 1022
6 Fréchet, J. M. J., Jiang, Y., Hawker, C. J. and Philippides, A. E. *Prepr. IUPAC Int. Symp. Functional Polymers, Seoul* 1989, 19
7 Hawker, C. J. and Fréchet, J. M. J. *J. Chem. Soc. Chem. Commun.* 1990, 1010
8 Hawker, C. J. and Fréchet, J. M. J. *J. Am. Chem. Soc.* 1990, **112**, 7638
9 Hawker, C. J. and Fréchet, J. M. J. *Macromolecules* 1990, **23**, 4726
10 Tomalia, D. A., Baker, H., Dewald, J., Hall, M., Kallos, G., Martin, S., Roeck, J., Ryder, J. and Smith, P. *Polym. J.* 1985, **17**, 117
11 Tomalia, D. A., Baker, H., Dewald, J., Hall, M., Kallos, G., Martin, S., Roeck, J., Ryder, J. and Smith, P. *Macromolecules* 1986, **19**, 2466
12 Newkome, G. R., Yao, Z., Baker, G. R. and Gupta, V. K. *J. Org. Chem.* 1985, **50**, 2004
13 Newkome, G. R., Baker, G. R., Saunders, M. J., Russo, P. S., Gupta, V. K., Yao, Z. and Bouillion, J. E. *J. Chem. Soc. Chem. Commun.* 1986, 752
14 Newkome, G. R., Yao, Z., Baker, G. R., Gupta, V. K., Russo, P. S. and Saunders, M. J. *J. Am. Chem. Soc.* 1986, **108**, 849
15 Denkewalter, R. G., Kolc, J. and Luskasavage, W. J. US Patent 4 289 872 (1981)
16 Padias, A. B., Hall Jr., H. K., Tomalia, D. A. and McConnell, J. R. *J. Org. Chem.* 1987, **52**, 5305
17 Hall, H. K. and Polis, D. W. *Polym. Bull.* 1987, **17**, 409
18 Aharoni, S. M., Crosby, C. R. and Walsh, E. K. *Macromolecules* 1982, **15**, 1093