One-Pot Synthesis of Hyperbranched Polyethers

K. E. Uhrich, C. J. Hawker, and J. M. J. Fréchet*

Department of Chemistry, Baker Laboratory, Cornell University,
Ithaca, New York 14853-1301

S. R. Turner

Corporate Research Laboratories, Eastman Kodak Company,
Rochester, New York 14650-2110

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ABSTRACT: A one-pot synthesis of a hyperbranched polyether using a A_2B type monomer under mild conditions is described. The monomer, 5-(bromomethyl)-1,3-dihydroxybenzene, undergoes self-condensation in the presence of potassium carbonate and 18-crown-6 to give polymers with weight-average molecular weights exceeding 10^5. Spectroscopic analysis of the hyperbranched polymers reveals that both O-alkylation and C-alkylation occurs during polymerization. The polymers contain a large number of phenolic hydroxyl groups located both at chain ends and at monomer units involved in irregular growth. The phenolic groups of the hyperbranched polyethers can be modified readily and completely by simple acylation, benzylation, or silylation processes. Comparison of the size-exclusion chromatography data with absolute molecular weight measurements by low-angle laser light scattering supports the proposed hyperbranched structure of the polyethers.

Introduction

In 1952, Flory postulated that highly branched polymers can be synthesized from A_2B type monomers without the occurrence of gelation.[1] These monomer units are of particular interest in the construction of highly branched polymers, as there is a potential branch point at each monomer unit.

Hyperbranched, or dendritic, macromolecules have been synthesized by various methods.[2] Our early involvement with dendritic macromolecules focused on a novel convergent growth scheme that afforded monodispersed products[3] with molecular weights up to 84 000. Similar approaches have been used to prepare polyamides,[4] polyphenylenes,[4] and polyesters.[5] A major advantage of the convergent-growth methodology in all of these preparations is that monodispersed, highly branched macromolecules with well-defined structures are obtained. However, this methodology involving stepwise growth is relatively costly and ill-suited for the rapid preparation of large amounts of polymers.

Hyperbranched macromolecules have also been prepared by a one-step method first introduced by Kim and Webster[6] in 1990. For example, a hyperbranched polyphenylene was obtained from 3,5-dibromophenylboronic acid via a palladium-catalyzed aryl coupling reaction. The resulting hyperbranched polymers had relatively low molecular weights (ca. 4000) with polydispersities of 2–3 and irregular structures. However, unlike linear polyphenylenes, these hyperbranched polymers were highly soluble in most organic solvents. The use of A_2B monomers to produce other hyperbranched macromolecules by "one-pot" processes, such as polyamines,[7] poly(siloxysilanes),[8] and polyesters[9] has been reported. A preliminary report on the synthesis of polyethers has also appeared.[10]

This report concerns the use of an A_2B monomer, 5-(bromomethyl)-1,3-dihydroxybenzene, in the one-pot preparation of a hyperbranched benzylic polyether.

Experimental Section

General Directions. Infrared spectra were recorded on a Nicolet IR/44 spectrometer as thin films on KBr disks. ^{1}H-NMR spectra were recorded on solutions in acetone-d_6 or $CDCl_3$ on a Bruker WM300 (300-MHz) spectrometer with the solvent proton signal as the standard. ^{13}C-NMR spectra were recorded at 75 MHz on a Bruker WM300 spectrometer on solutions in $CDCl_3$ or acetone-d_6 with the solvent carbon signal as the standard. Differential scanning calorimetry was performed on a Mettler DSC-10 standard cell calorimeter. Thermogravimetric analysis was performed on a Mettler TG50 Thermobalance.

Analytical TLC was performed on commercial Merck plates coated with silica gel GF_{254} (0.25 mm thick). Silica for flash chromatography was Merck Kieselgel 60 (230–400 mesh). Size-exclusion chromatography was carried out on a Nicolet LC/9560 liquid chromatograph connected to a Milton Roy refractoMonitor IV refractive index detector; data analysis was performed using Viscotek GPC-Pro software. Five 10-μm PL-gel GPC/SEC columns (300×7.7 mm) connected in series in order of decreasing pore size (type B to F) were used with THF as solvent. Size-exclusion chromatography for low-angle laser light scattering (LALLS) was carried out on four 7.5 mm i.d. × 300 mm, 10-μm-particle-diameter PL-gel mixed-bed columns coupled in series using THF as solvent. Columns were calibrated using narrow-dispersity polystyrene standards.

Benzyl bromide, dimethylformamide, and dichloromethane were purified by distillation. Acetone was distilled and stored over dry potassium carbonate. Potassium carbonate and cesium carbonate were heated to 120 °C over P_2O_5 under vacuum.

Caution! Hypersensitivity to 5-(bromomethyl)-1,3-dihydroxybenzene (1) may develop upon repeated exposure. Contact with the skin may result in a burning sensation accompanied by reddening of the contacted area. This may lead to a persistent rash. Exposure to this compound is to be avoided.

5-(Bromomethyl)-1,3-dihydroxybenzene (1). Triphenylphosphine (14.2 g, 54.3 mmol) was added slowly to a solution of 1,3-dihydroxy-5-(hydroxymethyl)benzene (6.89 g, 49.2 mmol) and carbon tetrabromide (18.1 g, 54.5 mmol) in freshly distilled THF (30 mL) under nitrogen. After 2 h, the reaction mixture was evaporated to dryness and the product purified by flash chromatography using 1:1 diethyl ether/dichloromethane as the eluent to give 1 as a white solid (6.84 g, 69% yield): ^{1}H NMR ($CDCl_3$) δ 4.35 (t, 2 H, CH_2Br), 6.28 (t, 1 H, Ar*H*), 6.45 (d, 2 H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 33.4 (CH_2Br), 107.3, 109.3 (ArCH), 139.4, 157.1 (ArC).

General Procedure for the Polycondensation of 1 under Slow Addition Conditions To Give Polyether 3. Monomer 1 (0.48 g, 2.4 mmol) in acetone (5 mL) was added via a syringe pump over a 3-h time period to a suspension of potassium carbonate (0.98 g, 7.1 mmol) and 18-crown-6 (0.06 g, 0.2 mmol) in acetone (5 mL) and heated to reflux under nitrogen. The reaction flask and syringe were covered with foil as the monomer is light sensitive. After the polymerization was complete, an

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excess of benzyl bromide and potassium carbonate was added. After 12 h, the reaction mixture was evaporated to dryness, redissolved in dichloromethane, washed with water (3×), dried over $MgSO_4$, and concentrated to give 0.30 g of a brown oil. The polymer was precipitated into diethyl ether from dichloromethane and collected by filtration to give polyether **3** as a light brown solid (0.15 g, 30% yield): IR 1600, 1450, 1380, 1150, 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.9–4.1 (br, 1 H, $PhCH_2Ph$), 4.3–5.1 (br, 7 H, $PhCH_2O$), 6.1–6.7 (br, 5 H, ArH), 6.7–7.5 (br, 14 H, ArH); ^{13}C NMR ($CDCl_3$) δ 26.8 ($PhCH_2Ph$), 70.1 ($PhCH_2O$), 101.6, 106.4 (ArCH), 127.5, 128.0, 128.6 (PhCH), 136.8, 139.2, 160.1 (Ar and Ph *C*).

General Procedure for the Polycondensation of 1 under Standard Conditions. A suspension of monomer **1** (0.51 g, 2.5 mmol), potassium carbonate (1.0 g, 7.5 mmol), and 18-crown-6 (0.04 g, 0.2 mmol) in acetone (8 mL) was heated to reflux under nitrogen in a foil-covered flask. After 51 h, an excess of benzyl bromide was added. After 12 h, the reaction mixture was evaporated to dryness, redissolved in dichloromethane, washed with water (3×), dried over $MgSO_4$, and concentrated to give 0.51 g of a yellow oil. The polymer was precipitated into diethyl ether from dichloromethane and collected by filtration to give polyether **3** as a yellow solid (0.32 g, 60% yield): IR 1600, 1450, 1370, 1160, 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.9–4.3 (br, 1 H, $PhCH_2Ph$), 4.4–5.3 (br, 8 H, $PhCH_2O$), 6.0–6.8 (br, 6 H, ArH), 6.8–7.7 (br, 20 H, ArH); ^{13}C NMR ($CDCl_3$) δ 27.1 ($PhCH_2Ph$), 70.1 ($PhCH_2O$), 101.6, 106.4 (ArCH), 127.1, 127.5, 128.0, 128.5 (PhCH), 136.8, 139.1, 160.2 (Ar and Ph *C*).

Alternately, after 51 h, the excess potassium carbonate was filtered from the reaction mixture and washed with acetone. The reaction solution was concentrated, precipitated into diethyl ether, and collected by filtration to give polyether **2** as a yellow solid (0.16 g, 53% yield): IR 3380, 1600, 1450, 1400, 1330, 1300, 1150, 1000 cm^{-1}; ^1H NMR (acetone-d_6) δ 2.7–3.4 (br, 3 H, OH), 3.6–4.2 (br, 1 H, $PhCH_2Ph$), 4.5–5.2 (br, 4 H, $PhCH_2O$), 5.7–7.0 (br, 8 H, ArH); ^{13}C NMR (acetone-d_6) δ 26.1 ($PhCH_2Ph$), 70.2 ($PhCH_2O$), 100.9, 102.1, 102.7, 106.0, 106.6, 106.7, 107.3, 107.7, 108.1, 109.2 (ArCH), 140.5, 140.7, 157.1, 159.0, 159.4, 161.0 (ArC).

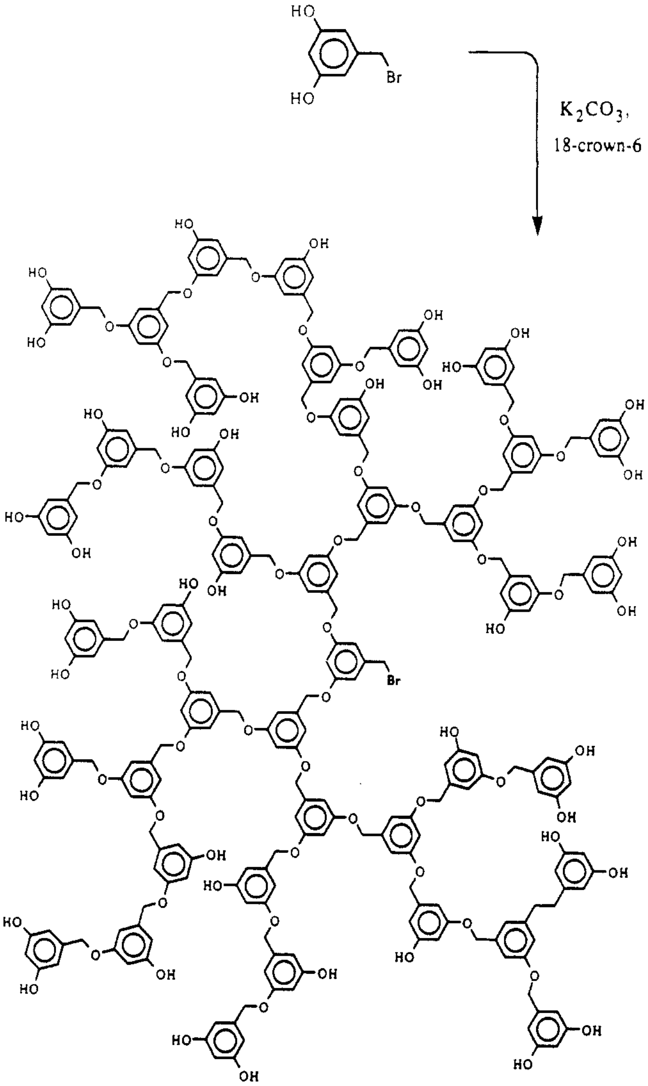
General Procedure for the Acetylation of Phenolic Polyethers 2 To Give Polymer 4. Acetic anhydride (0.37 g, 3.9 mmol) was added to a solution of polyether **2** (0.10 g), DMAP (0.05 g, 0.5 mmol), and triethylamine (0.54 mL, 3.9 mmol) in acetone (5 mL), and the reaction mixture was stirred at room temperature under nitrogen. After 16 h, the mixture was evaporated to dryness, redissolved in dichloromethane, washed with H_2O (3×) and brine, dried over $MgSO_4$, and evaporated to dryness. The polymer was purified by precipitation into hexane from dichloromethane to give polymer **4** as a brown solid (0.12 g, 86% yield): IR 2930, 1780, 1600, 1450, 1370, 1300, 1220, 1130, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.0–2.5 (br, 31 H, CH_3CO), 3.6–4.1 (br, 1 H, $PhCH_2Ph$), 4.5–5.2 (br, 21 H, $PhCH_2O$), 6.2–7.2 (br, 36 H, ArH).

General Procedure for the Silylation of Phenolic Polyethers 2 To Give Polymer 5. *tert*-Butyldimethylsilyl chloride (1.5 g, 10 mmol) was added to a solution of phenolic polyether **2** (0.30 g) and triethylamine (2.0 mL, 27 mmol) in DMF (5 mL) and heated to 80 °C under nitrogen. After 19 h, the reaction mixture was evaporated to dryness. The polymer was purified by precipitation into hexane from chloroform to give polymer **5** as a yellow solid (0.37 g, 63% yield): IR 2920, 2620, 2500, 1680, 1480, 1450, 1400, 1170, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.3–0.3 (br, 46 H, $SiCH_3$), 0.4–1.1 (br, 68 H, CCH_3), 3.6–4.1 (br, 2 H, $PhCH_2Ph$), 4.6–5.1 (br, 13 H, $PhCH_2O$), 5.9–6.8 (br, 19 H, ArH), 7.4–7.75 (m, 5 H, ArH).

Results and Discussion

The etherification chemistry utilized previously in the preparation of monodispersed polyethers by the convergent-growth approach[3] was adapted for this one-pot synthesis. The convergent-growth approach relied on a stepwise coupling-activation procedure for polymer growth involving 1,3-dihydroxy-5-(hydroxymethyl)benzene (**6**). In this process, the hydroxy groups of **6** are first coupled with a dendritic fragment and then the benzylic alcohol is brominated to give a reactive benzylic bromide which can be coupled with another monomer unit **6**. Monomer **6** was modified to allow for its self-condensation to give hyperbranched polyethers (Scheme I).

Scheme I



The monomer 5-(bromomethyl)-1,3-dihydroxybenzene (**1**) has been reported by Reimann,[11] who carried out the bromination of **6** with phosphorus tribromide to give **1**. However, compound **1** obtained by this method proved to be unstable due to the presence of acid generated in situ. Alternately, **6** can be brominated by carbon tetrabromide and triphenylphosphine and readily purified by flash chromatography. Under these reaction conditions, monomer **1** is relatively stable in the absence of light and air if kept at low temperature (0 °C). No self-condensation of **1** is observed in the absence of an activating reagent such as potassium carbonate.

In order for an A_2B polycondensation to proceed as postulated by Flory,[1] equal or near-equal reactivity of the two "A" reactive groups at all stages of the growth is preferred. This is expected to be the case given the meta-substitution pattern of monomer **1**.

Two methods of preparation of the hyperbranched macromolecules **3** were explored. In the first method, the possibility of controlling the growth of the macromolecule by changing the rate of monomer addition to the activating reagent, potassium carbonate, was explored. Alternately, the polyethers may also be prepared under a second procedure ("standard conditions") with simple mixing of all of the activating reagent and all of the monomer.

Table I
High Dilution Conditions: Effect of Monomer Addition Time[a]

addition time (h)	$\bar{M}_w$	$\bar{M}_n$	yield (%)	C-alkylation (%)
12	23 900	14 200	30	32
40	28 500	14 500	54	28

[a] Polycondensations performed with K_2CO_3 in acetone at 56 °C.

Slow Monomer Addition Method. The slow addition of monomer 1 to a reaction vessel containing potassium carbonate could conceivably lead to the preferential condensation of monomer with the growing macromolecule, thereby affecting directly $\bar{M}_w$ but not $\bar{M}_n$.

Though equal reactivity of all functional groups is essentially maintained, whether located on growing oligomers or on monomers, the statistics of growth may be affected by the relative concentrations of reactive species. As the reaction proceeds, lower concentrations of monomer units in the reaction mixture should favor additions to existing oligomers rather that new initiation processes; this, in turn, will affect $\bar{M}_w$. Therefore, addition of monomer 1 to the reaction mixture containing potassium carbonate and 18-crown-6 dispersed in acetone was carried out slowly using a syringe pump with a decreasing gradient of concentration. In some cases, to facilitate the subsequent characterization of the polyethers by spectroscopy and size-exclusion chromatography (SEC), an excess of benzyl bromide was added to 2 in order to alkylate any remaining phenolic groups. The fully benzylated product 3 was then purified by precipitation into diethyl ether. This precipitation step resulted in removal of low molecular weight materials from the isolated polymers. The discussion below and results reported in the tables refer only to the precipitated, therefore fractionated, portion of the alkylated reaction mixtures with structure 3.

Faster or slower, monomer addition times did not appear to have any appreciable effect on the molecular weights and polydispersities of the polyethers (Table I) as measured by SEC, although longer addition times afforded higher yields of isolated material. The extent of C-alkylation (ca. 30%), as measured by ^{1}H-NMR spectroscopy, is not influenced by the rate of monomer addition.

Standard Conditions. As the rate of addition of the monomer to potassium carbonate does not appear to have a significant effect on the characteristics of the isolated product, further studies were performed by concurrent one-time addition of all reagents. Once the time allowed for the reaction was reached, an excess of benzyl bromide was added to end-cap any remaining phenolic groups and the benzyl-terminated polymers 3 were purified by precipitation into diethyl ether. In some experiments only a portion of the reaction mixture was benzylated to allow for further comparisons of polymers having structures 2 and 3. For the unalkylated materials, workup of the reaction mixture included precipitation of the phenolic polymer 2 dissolved in methanol into diethyl ether. Using this procedure the yields of isolated polymer 2 were approximately the same as those reported for the benzyl-terminated polyether 3.

The influence of factors such as solvent and time of reaction on the resulting polyethers was explored. For example, in the preparation of 3, polar aprotic solvents such as acetone and 3-methyl-2-butanone afforded higher molecular weight polyethers than less polar solvents such as dichloroethane (Table II). The use of acetone was particularly advantageous, as higher yields of materials were obtained after precipitation. The extent of C-alkylation (ca. 20%) as measured by ^{1}H-NMR spectroscopy for both polymers 2 and 3 is not affected by the solvent but was found to be lower than the amount of C-alkylation in the polyethers synthesized under slow addition conditions (Table I).

Table II
Standard Conditions: Effect of Solvent on Polymer 3[a]

solvent	temp (°C)	$\bar{M}_w$	$\bar{M}_n$	yield (%)	C-alkylation (%)
dichloroethane	83	4 200	2 800	38	
3-methyl-2-butanone	94	12 600	3 500	39	24
acetone	56	29 300	14 700	73	16

[a] Polycondensations performed with K_2CO_3 over 18 h.

Table III
Standard Conditions: Effect of Reaction Time on Polymer 3[a]

reaction time (h)	$\bar{M}_w$	$\bar{M}_n$	yield (%)	C-alkylation (%)
18	22 700	6 900	46	10
51	41 700	12 300	60	16
92	49 600	8 500	66	11

[a] Polycondensations performed with K_2CO_3 in acetone at 56 °C.

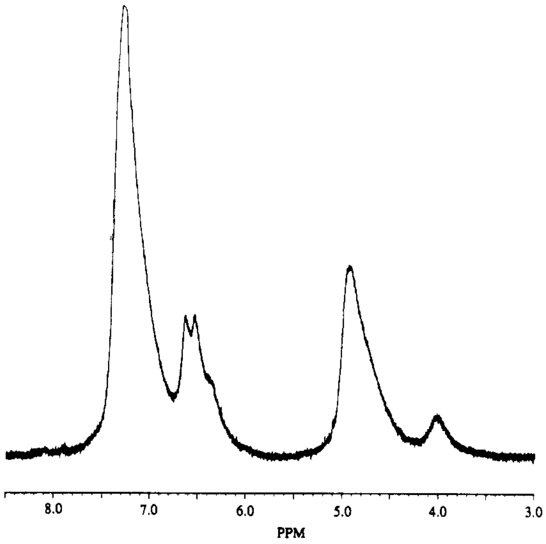


Figure 1. ^{1}H-NMR spectrum of polyether 3 synthesized via the one-pot process.

As expected, longer reaction times in acetone afforded polymers with higher molecular weights though the extent of C-alkylation remained unaffected (Table III). However, the ultimate molecular weights as determined by SEC did not exceed ca. 50 000 regardless of the reaction time.

Characterization. The ^{1}H-NMR spectrum of polyether 3 confirms its general structure (Figure 1). Hyperbranched polyether 3 shows signals that correspond to those of the more regular dendritic polyethers prepared by the convergent-growth approach.[3] For example, the benzylic protons resonate around 5.0 ppm and the aromatic protons around 6.7 and 7.4 ppm. However, the high molecular weight and broad molecular size distribution of polymer 3 synthesized by the one-pot method led to significant peak broadening in its ^{1}H-NMR spectrum.

In addition, the ^{1}H-NMR spectrum of polyether 3 shows a broad peak centered at 4.0 ppm corresponding to C-alkylation. This peak is not found in the spectrum of the polyethers prepared by the convergent-growth approach,[3] as the method for their preparation was optimized for the exclusive formation of C–O ether bonds rather than C–C bonds. In addition, it must be emphasized that the dendritic polyethers were purified at each step of growth.

Table IV
Comparison of Molecular Weights of Polymer 3 As Determined by SEC and LALLS Analyses

polymer	SEC: $\bar{M}_w$	SEC: $\bar{M}_n$	LALLS: $\bar{M}_w$
1	23 900	14 200	105 000
2	28 500	14 500	118 000
3	22 700	6 900	124 000

Integration of the methylene signal at 4.0 ppm relative to the O-alkylated methylene signal at 5.0 ppm indicates that C-alkylation accounts for up to 30% of the polyether structure, depending on reaction conditions.

^{13}C-NMR spectroscopy confirms the occurrence of C-alkylation with benzylic carbon signals observed at 27 ppm, in contrast to the benzylic carbon signals for O-alkylation at 70 ppm. Due to the complex structure of these polyethers, there is a significant overlap and broadening of the carbon resonances. However, the observed resonances confirm the general features of the polyethers, with aromatic carbons resonating near 110, 140, and 160 ppm.

Size-exclusion chromatography, using narrow molecular weight polystyrene standards, was used routinely in the analysis of benzyl-terminated hyperbranched polyether 3. For purposes of comparison, the weight-average molecular weights of several representative polyether samples were measured using LALLS. The values of absolute molecular weights obtained by LALLS measurements are generally 3–5 times higher than the relative values measured by SEC (Table IV). This is in qualitative agreement with previous observations[3] for dendritic polyethers prepared by the convergent-growth approach. The correlation between actual and SEC molecular weights having been established, all further discussions will refer to the more readily accessible SEC measurements which also provide valuable information on molecular weight distribution profiles.

Several LALLS traces display high molecular weight tails extending to $\bar{M}_w$ values exceeding 10^6. These tails, accounting for only a very small percentage of the total polymer, could easily be distinguished from the relatively narrow peaks of the bulk of the product and did not have a significant effect on the calculated $\bar{M}_w$ values.

The broad polydispersity of these hyperbranched polyethers may be partially accounted for by the presence of both *linear* and *branched* repeating units in structures 3 and 2 as shown in Scheme I. In order to simplify the overall representation Scheme I only shows the O-alkylated material; C-alkylation occurs to varying degrees as shown in the tables. As a result of C-alkylation the hyperbranched structure may actually contain some units resulting from an AB_3 type polycondensation reaction. The *linear* units arise from reactions involving only one of the two phenolic groups of monomer 1 or corresponding oligomeric structures. The degree of branching of the polyethers reported herein cannot be ascertained in simple fashion due to the occurrence of C-alkylation which provides for a new mode of branching in polymers 2 and 3. Previous studies on analogous polymers prepared by a variety of one-step procedures have led to hyperbranched structures with degrees of branching varying from 40 to 60%.[6,9]

The possible incorporation of carbonates or aldol condensation products into the hyperbranched polyethers was investigated, as polycarbonates have been synthesized from benzylic bromides in the presence of potassium carbonate with catalytic amounts of various crown ethers in organic solvents.[12] The incorporation of carbonyl functionalities in the hyperbranched polymers 2 and 3 can be excluded on the basis of infrared spectroscopy, as no absorption peaks indicative of a carbonate C═O stretch at 1745–1750 cm^{-1} or a C–O stretch at 1235–1280 cm^{-1} are observed.

The structures proposed for polymers 2 and 3 are supported by infrared spectroscopy, which shows strong absorption peaks for the ether C–O stretches at 1150 cm^{-1} and the aromatic C–C stretches at 1600 and 1450 cm^{-1}. In benzylated polymer 3, no absorption peak corresponding to the phenolic O–H stretch is observed.

Functionalization. The self-condensation of monomer 1 described above results in the formation of a hyperbranched polymer 2 with phenolic chain ends. As was shown with the preparation of 3, these multiple chain ends have a high reactivity and can be modified into the corresponding benzylic ethers. Similarly, the solubility of 2 in aqueous base indicates that the conversion of the chain ends to the corresponding phenolate moieties occurs readily.

The phenolic groups of polyether 2 can also be functionalized to give terminal acetyl and silyl groups. These modifications change the solubility of polyether 2 and may be useful in its characterization. Acetylation of phenol-terminated polyether 2 with acetic anhydride, triethylamine, and (dimethylamino)pyridine in acetone gave the acetyl-terminated polyether 5 in 86% yield after purification. The absence of the phenolic O–H stretch at 3300 cm^{-1} indicates that functionalization was complete. Similarly, treatment of polyether 2 with *tert*-butyldimethylsilyl chloride and triethylamine in DMF gave silyl-terminated polyether 5 in 63% yield after purification. Again, the absence of the phenolic O–H stretch at 3300 cm^{-1} indicates exhaustive functionalization of the phenolic groups. In contrast to the phenol-terminated polyethers 2 which were soluble in alcohols, aqueous base, or highly polar aprotic solvents such as DMF, the functionalized polyethers 3–5 are soluble in a variety of organic solvents such as chloroform or toluene.

The ^{1}H-NMR spectra of the functionalized polyethers are in agreement with the proposed structures. Benzyl-terminated polymer 3 shows several broad resonances in the aromatic region from 6.2 to 7.6 ppm (Figure 1). The aromatic protons corresponding to the benzylic chain ends are seen as a peak centered at 7.2 ppm. Due to the broadness of the peaks, some overlap is seen between these and the signals for the aromatic protons of the repeat units derived from 1. For acetyl-terminated polymer 4, the signals for the aromatic protons of the repeating units range from 6.3 to 7.1 ppm, while the resonance for the methyl protons of the acetate is seen near 2.3 ppm. For the silyl-terminated polyethers 5, the aromatic protons of repeat units not containing a silyl ether resonate from 6.3 to 6.6 ppm and aromatic protons of the silylated repeat units are observed from 7.4 to 7.7 ppm. The silylmethyl protons resonate at 0 and 0.9 ppm.

As expected, molecular sizes of the hyperbranched polymers are affected by their functionalization. This can easily be observed by the increase in hydrodynamic volume. The molecular weights as determined by SEC roughly correlate to the theoretical molecular weights calculated for the different functionalizations (Table V).

Differences in the thermal properties of hyperbranched polymers 2–5 were studied by differential scanning calorimetry (Table VI). The phenol-terminated polyethers 2 have the lowest glass transition temperatures, near 311 K. The benzyl-terminated polyethers 3 have glass transition temperatures around 324 K. This is in close agreement with the T_g (316 K) observed for the regular

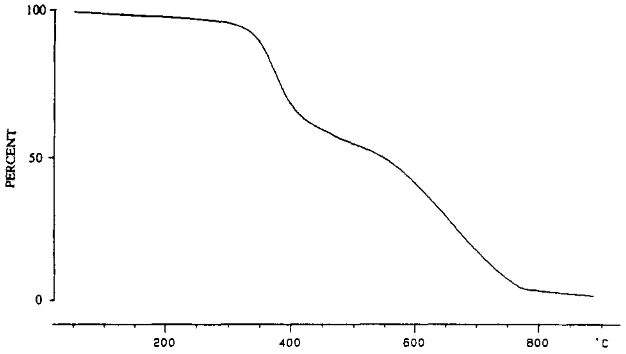


Figure 2. Thermogravimetric analysis curve of a benzylated polyether 3 heated under nitrogen.

Table V
Effect of Functionalization on the SEC Molecular Weights of Polyethers

functional group	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w$ (calc)
hydroxy	6 500	5 000	6 500
acetyl	6 200	4 200	7 600
benzyl	9 800	5 700	8 900
silyl	14 000	7 400	9 600

Table VI
Effect of Functionalization on Glass Transition Temperatures

functional group	T_g (K)	functional group	T_g (K)
hydroxy	311	benzyl	324
acetyl	343	silyl	343

dendritic polyethers obtained by the convergent-growth approach. Both the acetyl- (**4**) and silyl-terminated (**5**) polyethers have glass transition temperatures near 343 K.

The thermal properties of the benzyl- and phenol-terminated polyethers were also studied by thermogravimetric analysis (TGA). A representative TGA curve of a benzylated polyether **3** measured under a nitrogen atmosphere is shown in Figure 2. A 3.9% weight loss seen between room temperature and 300 °C may be due to residual solvent retained in the hyperbranched polymer **3**. The onset of decomposition is seen near 315 °C with 40% weight loss at 470 °C, 56% at 760 °C, and less than 1% residue remaining at 800 °C.

For the phenol-terminated polyethers **2**, a faster rate of decomposition is seen in the TGA curve. A weight loss of 25% is seen between room temperature and 400 °C, with 69% loss at 750 °C and 5% residual material at 890 °C. The use of air rather than nitrogen as the flushing gas did not alter the rate or onset temperature of decomposition in polyethers **2** and **3**.

Conclusion

The polycondensation of the A_2B monomer, 5-(bromomethyl)-1,3-dihydroxybenzene (**1**), via a one-pot approach has been shown to be a practical route for the formation of hyperbranched polyethers. Although the polymers that are obtained have irregular structures incorporating both O-alkylated and C-alkylated branched units as well as linear units, the SEC and LALLS data support a globular structure. The main advantage of the one-pot method is its simplicity, which allows for rapid access to larger amounts of high molecular weight hyperbranched materials.

The phenolic groups of the polyethers are readily functionalized in quantitative fashion, confirming the accessibility of the chain ends. These functionalization experiments also confirm that the properties of the hyperbranched macromolecules are largely determined by the nature of their chain ends.

The synthesis of these hyperbranched macromolecules still needs to be refined to give better control over variables such as molecular weight, polydispersity, and degree of branching. We have recently developed a new silicon-assisted polyether synthesis[13] that is useful in the preparation of high molecular weight polyethers and may be applicable to the more controlled preparation of hyperbranched structures. However, no further studies are contemplated with monomer **1** which appears to have powerful allergenic properties, but new monomers with increased stabilities are under investigation.

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