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Synthesis of dendritic poly(arylene ether)s from a linear polymer core

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Abstract

Three generations of dendritic poly(arylene ether)s with terminal 4-fluorophenylthio- or 4-fluorophenylsulfonyl groups have been synthesized. A new relatively high molecular weight bisphenol containing two pendent 4-fluorophenylthio groups was converted to a poly(arylene ether sulfone) to act as the dendritic core. A divergent approach with an activation/condensation sequence was used. The pendent 4-fluorophenylthio groups in the base polymer were oxidized with H_2O_2 in formic acid to give 4-fluorophenylsulfonyl groups in which the fluoride groups are then activated toward nucleophilic displacement reactions. The condensation step involved the reaction of a phenol containing two pendent 4-fluorophenylthio groups with the activated core polymer in the presence of Cs_2CO_3. Reiteration of these steps gave the subsequent generations. The polymers have high thermal stabilities by TGA analysis (5% weight loss > 500 °C).

Keywords: Dendritic polymers; Polyetherification; Poly(arylene ether) core

1. Introduction

Since the early papers on dendrimers by Vogtle [1], Tomalia [2], and Newkome [3] several thousand papers have been published on the subject and several reviews of dendrimers have been written [4–9]. In a recent review article on dendronized polymers, Schluter [10] has pointed out that most of the effort on dendritic molecules has been directed toward dendrimers with small cores. Tomalia earlier reported the synthesis of a polymer core dendron [11] but until recently there has been little effort in this area [10,12–14]. Schluter [10] also pointed out that dendritic polymers are necessarily polydisperse since the polymer core is polydisperse. This would be especially true for step growth polymers. This eliminates the use of matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) as a method of analyzing these high molecular weight dendritic polymers since the ion current is spread over a very large number of molecules. Frechet [15] was recently able to surmount this problem by the use of a poly(*p*-hydroxystyrene) polymer core that had a very narrow molecular weight distribution (PD = 1.07).

In the previous work [16], we described the preparation of four generations of poly(arylene ether) dendrimers with terminal 4-fluorophenylthio- or 4-fluorophenylsulfonyl groups, and using bis(4-fluorophenyl) sulfone as the core. An aryl carbonate as a masked phenol was employed in the polyetherification step. Aryl carbamates have also been used as masked phenols in the etherification reactions [17]. They have the same advantages as aryl carbonates [17,18], i.e. easy cleavage and shorter reaction times since the dehydration step in the polymerization reaction is eliminated. Both of them are more stable and generally easier to purify than the parent phenols. Nuclear magnetic resonance (NMR) experiments were carried out for the identifications of the protons, and MALDI-TOF-MS was used for the mass determination of the dendrimers. With MALDI, along with ^{1}H and ^{13}C NMR, we were able to precisely determine the structures of the dendrimers through generation 4. This allowed us to define the optimum conditions for carrying out the condensation/activation steps employed in the syntheses.

We were interested in extending this methodology to the synthesis of dendrimers with a polymer core. The terminal activated fluoro groups on these polymers could potentially be converted to thiol groups [19] and the thiols then oxidized to the corresponding sulfonic acids [20]. Ion exchange membranes for use in fuel cells have been synthesized from sulfonated poly(aryl ether)s and found to have much shorter lifetimes than Nafion®-based materials [21], due to loss of mechanical properties presumably the result of scission of the polymer chains. We envisioned the synthesis of a polymer core membrane material in which the

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hydrophobic polymer core might give a more stable material since cleavage reactions at the pendent groups would not result in chain cleavage. The subject of mechanical properties in dendrimer materials has received little attention because of the very small quantities of materials generally used and also because the backbones utilized are not designed to be engineering materials.

We report herein the synthesis and characterization of dendritic poly(arylene ether)s, with terminal 4-fluorophenylthio or 4-fluorophenylsulfonyl groups, using a linear poly (arylene ether) core. An aryl carbamate and an aryl carbonate were employed for the preparation of the core and the dendrimers, respectively. Although MALDI-TOF-MS analyses could not be carried out due to the high molecular weight and polydispersity of the polymers, the NMR data along with a correlation with the data obtained previously [16] indicated that the proposed structures that were synthesized are correct.

2. Experimental

2.1. Chemicals

N, *N*-dimethylacetamide (DMAc, Aldrich) was dried over CaH_2 and distilled in vacuo; acetone (Fisher Scientific), anhydrous cesium carbonate (Aldrich), benzene (Fisher Scientific), carbon disulfide (Fisher Scientific), chloroform (Fisher Scientific), dichloromethane (Fisher Scientific), bis(4-fluorophenyl)sulfone (Aldrich), ethyl ether (Fisher Scientific), formic acid 95–97% (Aldrich), heptanes (BDH), hydrogen peroxide 30% (Aldrich), magnesium sulfate (Omega), methanol (Fisher Scientific), 1-methyl-2-pyrrolidinone (NMP, Fisher Scientific), petroleum ether (Fisher Scientific), phenol (A&C), phosphorus pentachloride (A&C), *n*-propylisocyanate (Aldrich), pyridine (Caledon), toluene (Fisher Scientific), triethylamine (Lancaster), triphosgene (bis(trichloromethyl) carbonate, Aldrich), and xylene (Caledon), reagent grade, were used as obtained.

2.2. Measurements

^1H and ^{13}C NMR spectra were recorded on Varian spectrometers, using chloroform-*d* ($CDCl_3$) and dimethylsulfoxide-d_6 (DMSO) as solvents. For spectroscopic results, chemical shifts are given in ppm against tetramethylsilane as an internal standard. High pressure liquid chromatography (HPLC) analyses were done with a Milton Roy CM4000 instrument with auto injector equipped with a Lichrosphere 5 RP18e column (250×4 mm^2), and UV detector (Milton Roy Spectro Monitor 3100) at 254 nm. Samples were eluted by methanol at a flow rate of 1.0 ml/min. Conventional mass spectra were recorded on Kratos MS 25 RFA and Du Pont 21-492B spectrometers. Molecular weights (M_n, M_w, number and weight-average molecular weights) and polydispersity ratios (M_w/M_n) were estimated by size exclusion chromatography (SEC) on a Waters 510 HPLC equipped with a set of three 5 μm polystyrene gel columns (Phenogel, 500 Å, 300×8 mm^2), and UV detector (Waters 441) at 254 nm. Samples were eluted by $CHCl_3$ at a flow rate of 1 ml/min. Calibration was achieved using polystyrene standards of narrow molecular weight distributions. The repeatability was about 10%. Glass transition temperatures (T_g) and degradation temperatures (T_d) of polymers were determined by differential scanning calorimetry and thermogravimetry, using a Seiko 220 instrument at a heating rate of 20 °C/min, under a stream of nitrogen at 160 and 200 ml/min, respectively. The values of T_g were recorded from the second scan and taken from the midpoint of the change in slope of the baseline. Inherent viscosities were determined for solutions of 0.5 g/dl in *N*-methyl-2-pyrrolidinone (NMP) at 25 °C with a #1 Ubbelohde viscometer. Efflux time of the solvent was about 160 s and the repeatability of the measurements about 5%.

2.3. Synthesis of monomers and polymers

2.3.1. Dichloro-bis[4-(4-fluorophenylthio)phenyl]methane **4**

Product **3** [16] (8.69 g, 20 mmol) and phosphorus pentachloride (6.25 g, 30 mmol) were added to a dry mixture of 40 ml of benzene and 8 ml of carbon disulfide. After refluxing the mixture for 24 h, the solvent was removed by slow distillation. The remaining material, a green liquid, was separated by distillation of by product $POCl_3$ (Kugelrohr) at 100 °C for 0.5 h. Compound **4** was obtained in 9.49 g (isolated yield = 97%; purity of the isolated product by HPLC = 87%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.50–7.42 (m, 4H, Ar *ortho* and *meta* to $-CCl_2-$), 7.12–7.04 (m, 4H, Ar *ortho* and *meta* to –F); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.87, 161.57, 141.74, 139.85, 136.18, 136.07, 130.84, 128.24, 127.57, 126.92, 117.15, 116.86.

2.3.2. Bis[4-(4-fluorophenylthio)phenyl], bis(4-hydroxyphenyl)methane **6**

The crude product **4** (8.81 g, 18 mmol) was mixed with distilled xylene (11 ml) under nitrogen and, while stirring vigorously, freshly distilled phenol **5** (8.47 g, 90 mmol) was added. The resulting mixture was slowly heated up to the boiling point of the xylene. Evolution of HCl then occurred. The reaction time was 3 h. After the addition of **4**, the reaction mixture became an intense violet color. When the reaction was finished, it was extracted with ethyl ether and the ethereal phase washed with water several times, dried with magnesium sulfate, and concentrated under vacuum. The red–orange solid obtained was stirred with triethylamine for 3 h. A beige-colored solid was separated by filtration and washed with heptanes. The treatment with triethylamine was repeated twice. Then, the solid was dissolved in CH_2Cl_2, dried with $MgSO_4$ and the solution filtered and concentrated. The concentrated solution was poured dropwise into petroleum ether. The solid that precipitated was separated by filtration and dried under vacuum at room

temperature. A light beige solid was recovered (8.7 g of **6**, isolated yield = 80%, purity of the isolated product by HPLC > 98%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.45–7.40 (m, $4H_{12}$, Ar *ortho* to –S and *meta* to –F), 7.06–6.94 (m, 16H, others Ar's), 6.65–6.75 (d, 4H, Ar *ortho* to –OH), 4.74 (s, 2H, –OH); ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.50, 161.20, 153.79, 145.61, 139.00, 135.07, 134.96, 134.75, 132.35, 131.87, 129.49, 128.29, 116.84, 116.55, 114.57, 63.15; MS (IE) *m/e*: 604 (MI), 511, 477, 401, 257.

2.3.3. Aryl carbamate *7*

To a 500 ml round-bottom flask fitted with a magnetic stirrer, reflux condenser, and a drying tube were added **6** (4.83 g, 8 mmol), toluene (200 ml), *n*-propylisocyanate (7.50 ml, 80 mmol), and triethylamine (0.10 ml). The reaction solution was heated at 100 °C, with stirring, for 24 h and, after cooling, the product was isolated by distillation of the liquid components under reduced pressure. The solid separated by filtration was dissolved in CH_2Cl_2, and the solution was filtered, concentrated and poured into 300 ml of petroleum ether. Filtration yielded 5.0 g of a white solid (purity of the isolated product by HPLC > 98%, isolated yield = 80%): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50–7.36 (m, $4H_{12}$, Ar *ortho* to S and *meta* to F), 7.18–6.94 (m, 20H, others Ar's), 4.95–5.10 (bs, 2H, –NH), 3.15–3.30 (m, 4H, $-NCH_2-$), 1.50–1.70 (m, 4H, $-CH_2-$), 1.00–0.90 (t, 6H, $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.50, 161.20, 154.74, 149.47, 144.95, 143.09, 135.20, 135.09, 131.90, 129.350, 128.30, 120.83, 116.89, 116.60, 63.67, 43.18, 23.29, 11.47; MS-FAB *m/e*: 775 (MI), 604, 511, 401, 307, 154, 136, 107.

2.3.4. Phenyl-4-hydroxyphenyl-bis[4-(4-fluorophenyl-sulfonyl)phenyl]methane *8*

Phenol **5** (188.2 g, 2.0 mol), 4,4′-bis(4-fluorophenylthio)-triphenylcarbinol [16] (29.22 g, 0.057 mol) and a catalytic amount of sulfuric acid were placed in a 1000 ml flask equipped with a condenser at 75 °C for 24 h (the reaction was followed by HPLC). When the reaction was complete, water (500 ml) was added and the mixture was stirred for 0.5 h. The organic phase, a viscous liquid, was separated and diluted with ethyl ether and extracted with 20% aqueous sodium hydroxide until the color faded in the aqueous phase. After that, the ethereal phase was washed several times with water, dried with anhydrous magnesium sulfate, filtered, and the ether evaporated under vacuum. The brown viscous liquid (purity by HPLC = 81%) that separated was purified by treating it with triethylamine (100–150 ml), under stirring for 3 h. After that, the mixture was filtered, and the white solid recovered was dissolved in $CHCl_3$ (200–300 ml), and the solution was filtered. It was then divided into 20–30 fractions. Each of these fractions was poured, dropwise, into petroleum ether under stirring and the solid obtained was separated by filtration. Large amounts of the white solid in petroleum ether must be avoided since it very easily becomes a gum. Vigorous stirring helps to transform the gum into solid form. The solids were collected, washed with petroleum ether, and dried at 40 °C under vacuum. After the workup, 20.1 g of **8** was obtained (purity of the isolated product by HPLC = 91%, isolated yield = 60%). Characterization results have been reported in Ref. [16].

2.3.5. Aryl carbonate *9*

A mixture of the crude phenol **8** (40 mmol, 23.55 g), pyridine (100 ml) and toluene (150 ml) was stirred under argon for 0.5 h at 40 °C. A solution of bis(trichloromethyl) carbonate (triphosgene, 10.00 mmol, 2.97 g) in toluene (50 ml) was added, dropwise, under the same conditions. The reaction was followed by HPLC. When the reaction was finished, it was poured into methanol (400 ml) and filtered. The solid was purified by fractional precipitation by dissolving the sample in chloroform (20 ml/g) and using methanol as the non-solvent. The white solid obtained was dried under vacuum at 60 °C. After the workup, 20.5 g of a white solid was obtained (isolated yield = 85%). The purity by SEC of the isolated product was 100%. Characterization results are reported in Ref. [16].

2.3.6. Poly(arylene ether sulfide) *P1*

A 25 ml Pyrex three-necked round-bottom flask equipped with a condenser, argon inlet/outlet, magnetic stirrer, and thermometer was charged with carbamate **7** (0.7749 g, 0.100 mmol), anhydrous Cs_2CO_3 (0.358 g, 1.1 mmol), bis(4-fluorophenyl)sulfone **10** (0.2543 g, 0.100 mmol) and DMAc (2 ml). Argon was sparged through the reaction mixture with stirring for 30 min, and then the mixture was kept at 140 °C, under argon, until a very viscous solution was obtained (~20 h). During the last 2 h, the temperature was increased to 160 °C. Heating was accomplished with a silicone oil bath. The reaction mixture was diluted with 5 ml of DMAc, and poured into 100 ml of methanol containing a few drops of HCl. The mixture was filtered, and the separated polymer was dissolved in $CHCl_3$. The solution was filtered, concentrated and the polymer precipitated out by adding the solution, dropwise, into CH_3OH. The polymer was collected by filtration and dried under vacuum at 80 °C. After the workup, 0.64 g (isolated yield = 78%) of polymer **P1** was obtained. This product was purified by reverse precipitation by dropwise addition of acetone (8 ml) to a solution of the polymer in $CHCl_3$ (15–20 ml). After separation of the polymer, it was dissolved in $CHCl_3$ precipitated in CH_3OH and dried under vacuum at 80 °C (0.45 g, isolated yield = 55%): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90–7.82 (d, $4H_1$), 7.46–7.34 (m, $4H_{12}$), 7.18–6.96 (m, 20H, others Ar's), 6.96–6.84 (d, $4H_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.60, 161.68, 161.30, 153.57, 144.48, 142.87, 135.97, 135.80, 135.55, 135.44, 132.76, 131.72, 130.01, 128.98, 128.08, 119.31, 118.32, 116.97, 116.68, 63.63.

2.3.7. Poly(arylene ether sulfone) *P2*

A typical experiment was conducted in a 25 ml round-bottom flask. **P1** (0.50 g) was suspended in 20 ml of 90%

formic acid with low stirring. The mixture was heated to 40 °C and 5.0 g of 30% aqueous hydrogen peroxide was added dropwise over 1 h. After the addition, the reaction mixture was stirred for 0.5 h. The product was filtered, washed with methanol and dried at 80 °C under vacuum to give **P2**. After the workup, 0.51 g of the product was obtained (isolated yield = 95%): ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04–7.92 (d, $4H_{14}$), 7.92–7.76 (m, $8(H_1 + H_6)$), 7.38–6.96 (m, 16H), 6.96–6.84 (d, $4H_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.28, 163.92, 161.40, 153.77, 151.97, 141.75, 139.64, 137.78, 136.15, 132.78, 132.08, 131.48, 131.34, 130.52, 127.96, 120.23, 119.05, 117.89, 117.59, 64.61.

2.3.8. Dendritic poly(arylene ether sulfide)'s, DLPg-S's

A 25 ml Pyrex three-necked round-bottom flask was equipped with a condenser, argon inlet/outlet, magnetic stirrer, and thermometer. The flask was charged with carbonate **9** (0.505 g, 0.420 mmol) along with the required starting material (**P2** (0.353 g, 0.400 mmol of repeat units), or DLP1-SO_2 (0.430 g, 0.200 mmol of repeat units), or DLP2-SO_2 (0.468 g, 0.100 mmol of repeat units)), anhydrous Cs_2CO_3 (0.137 g, 0.462 mmol), and DMAc (10–20 ml). Argon was sparged through the reaction mixture with stirring for 30 min, and then the mixture was kept at 140 °C, under argon, for 24 h. Heating was accomplished with a silicone oil bath. Then the reaction mixture was poured into 100 ml of methanol containing a few drops of HCl. The mixture was filtered, and the separated product was dissolved in $CHCl_3$. The solution was filtered, concentrated and the dendritic polymer DLP1-S, or DLP2-S, or DLP3-S precipitated out by adding the solution, dropwise, into CH_3OH. It was collected by filtration and dried under vacuum at 60 °C. The isolated yield was about 80% for all of them.

DLP1-S. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90–7.82 (d, $8H_1$), 7.82–7.74 (d, $4H_6$), 7.42–7.34 (m, $7H_{12}$), 7.34–6.92 (m, 54H, others Ar's), 6.92–6.84 (m, $9H_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.11, 162.22, 161.64, 153.12, 151.11, 146.14, 144.78, 143.41, 141.16, 140.66, 135.38, 135.30, 134.75, 132.95, 132.53, 131.86, 131.02, 130.43, 129.14, 128.16, 128.01, 127.37, 126.60, 119.65, 119.39, 118.65, 118.19, 116.89, 116.67, 64.09.

DLP2-S. ^{1}H NMR (400 MHz, CDCl): δ 7.92–7.82 (d, $15H_1$), 7.82–7.74 (d, $11H_6$), 7.42–7.34 (m, $16H_{12}$), 7.34–6.92 (m, 124H, others Ar's), 6.92–6.80 (m, $16H_3$); ^{13}C NMR data were similar to that of DLP1-S.

DLP3-S. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.82 (d, $30.7H_1$), 7.82–7.74 (d, $26H_6$), 7.44–7.34 (m, $31H_{12}$), 7.34–6.93 (m, 261H, others Ar's), 6.93–6.80 (m, $34H_3$); ^{13}C NMR data were similar to that of DLP1-S.

2.3.9. Dendritic poly(arylene ether sulfone)'s, DLPgSO_2's

The experiment was conducted in a similar way to that described for the synthesis of **P2**; but in this case, the starting material was DLP1-S, or DLP2-S, or DLP3-S. The isolated yield was 90% for all of them.

DLP1-SO_2. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00–7.72 (m, $27(H_{14} + H_1 + H_6)$), 7.38–6.94 (m, 47H, others Ar's), 6.94–6.80 (m, $8H_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.07, 164.52, 161.80, 153.73, 151.62, 144.54, 141.59, 140.49, 139.90, 137.40, 135.12, 132.68, 131.85, 130.96, 130.87, 130.70, 130.47, 128.56, 127.40, 127.25, 119.81, 118.43, 117.11, 116.88, 65.00.

DLP2-SO_2. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00–7.72 (m, $56(H_{14} + H_1 + H_6)$), 7.38–6.94 (m, 109H, others Ar's), 6.94–6.80 (m, $17H_3$); ^{13}C NMR data were similar to that of DLP1-SO_2.

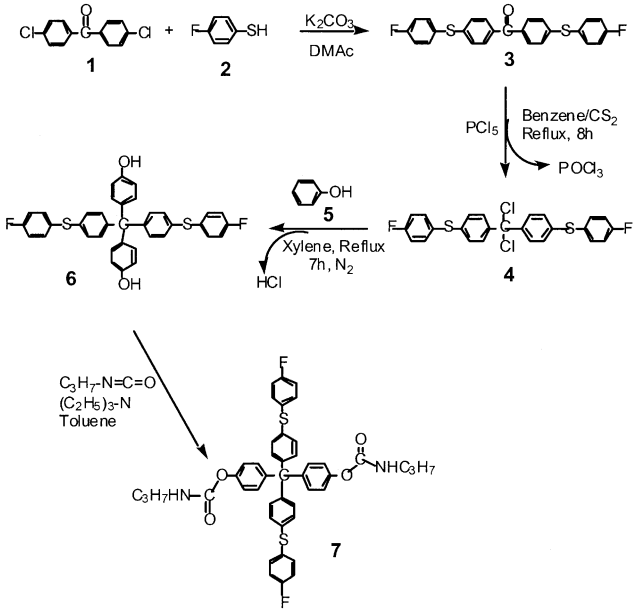
DLP3-SO_2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.70 (m, $121(H_{14} + H_1 + H_6)$), 7.40–6.94 (m, 227H, others Ar's), 694–6.80 (m, $34H_3$); ^{13}C NMR data were similar to that of DLP1-SO_2.

3. Results and discussion

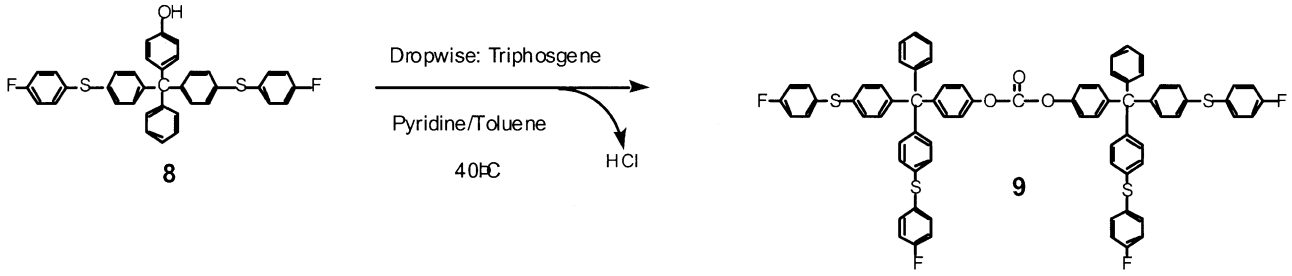
3.1. Syntheses of monomers and polymers

The synthesis of the three generations of dendritic poly (arylene ether)s was carried out using the divergent method based on a condensation/activation sequence, and a linear polymer as the core. The condensation reaction is a displacement reaction of an aryl halide activated by a sulfone group using a metal phenolate. The activation reaction was the oxidation of 4-fluorophenylthio moieties to 4-fluorophenylsulfonyl groups.

The first step of this research was the preparation of the new monomer **6** and its carbamate **7** (Scheme 1), and the synthesis of monomer **8** and its carbonate **9** (Scheme 2),

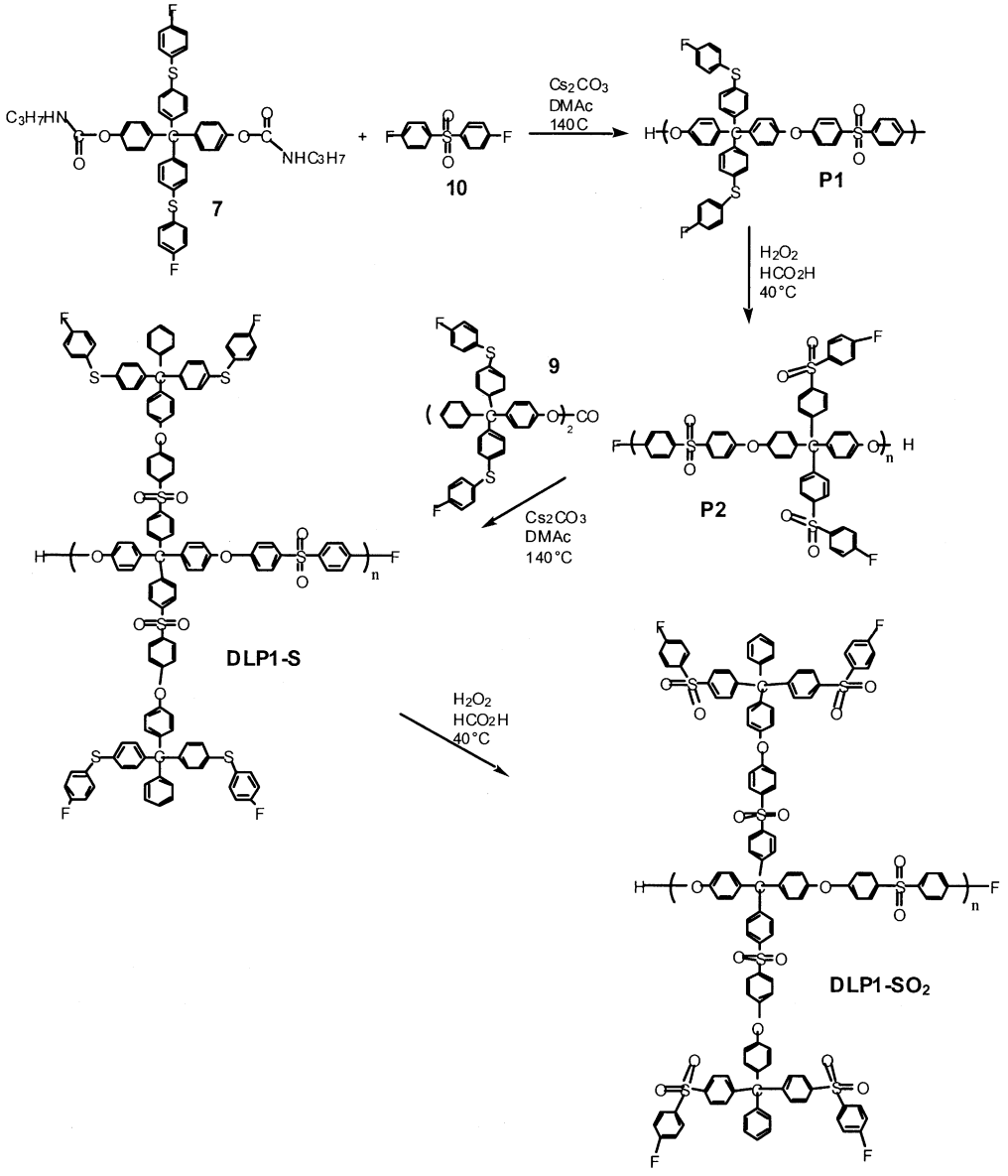


Scheme 1.

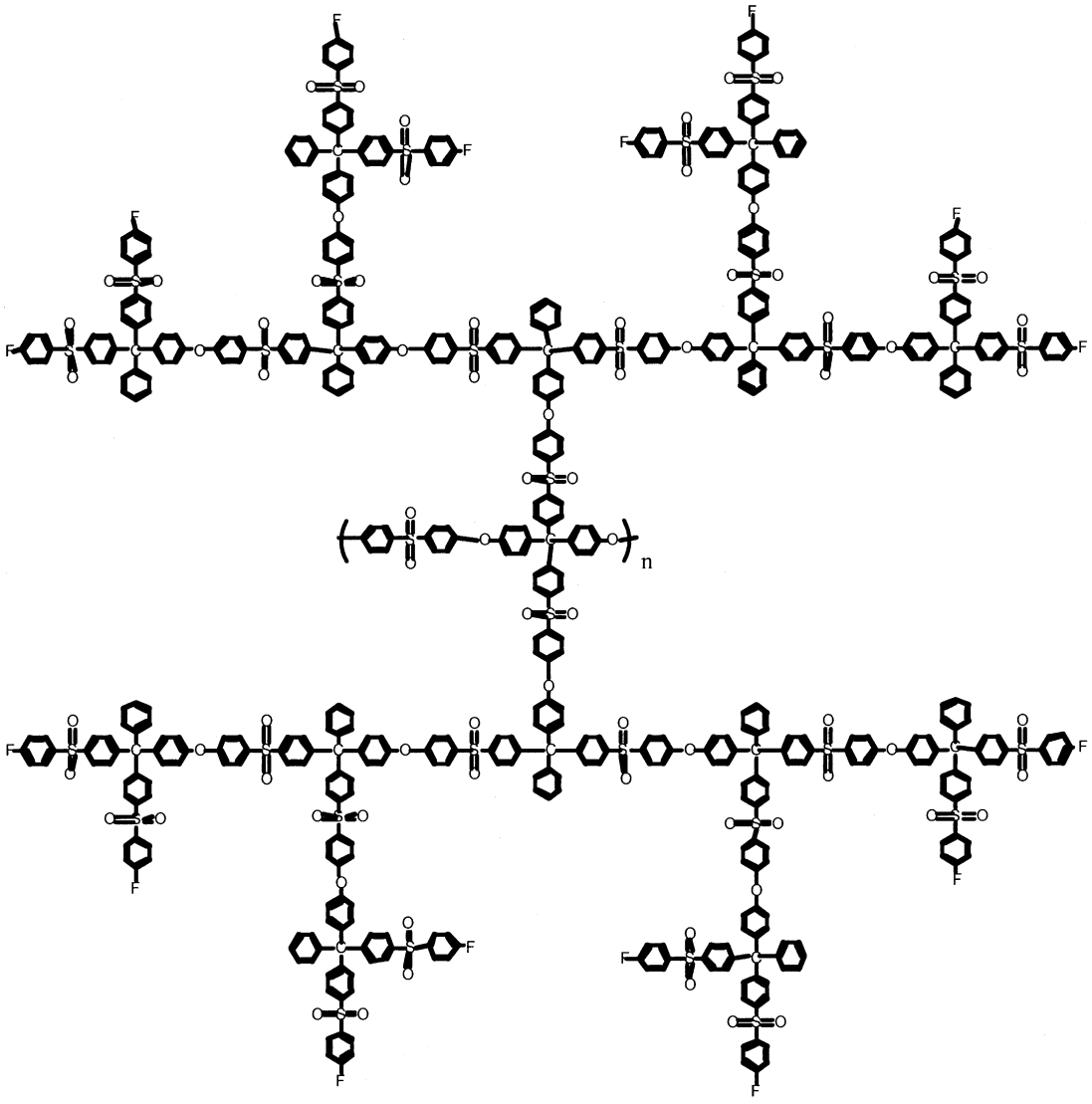


Scheme 2.

according to the procedure reported in the previous paper [16]. The purification procedure for phenol **8** was modified. Instead of employing a chromatographic column, it was treated with triethylamine for its purification. The separation procedure for **9** was also improved. The advantages of using triethylamine were that we could easily and rapidly obtain a relatively pure white product. Bisphenol **6** and phenol **8** should not be dried over 40 °C because they tend to decompose.



Scheme 3.



DLP3-SO_2

Scheme 4.

The synthesis of the new monomer **6** began with the displacement of the chloride groups of 4,4′-dichlorobenzophenone **1** with 2 mol of 4-fluorothiophenol **2** [22]. In the following reaction, the dichloride product **4** was formed from **3** using PCl_5 as the chlorinating agent. The dichlorinated product **4** was then reacted with 2 mol of phenol **5** in the presence of refluxing xylene [23] to produce the bisphenol **6**. The overall isolated yield of **6** from **1** was 54%. The purity by HPLC of **6** after treatment with triethylamine was 98%. The last reaction shown in Scheme 1 was the synthesis of the aryl carbamate **7** from bisphenol **6** using *n*-propylisocyanate [17,24]. The isolated yield and purity after purification of product **7** were 80 and 98% (HPLC), respectively. NMR and MS characterization of those products confirmed the proposed structures.

The linear poly(arylene ether sulfide) **P1** was synthesized from the aryl carbamate **7**, bis (4-fluorophenyl) sulfone **10**, with Cs_2CO_3 as the condensation agent (Scheme 3). The yield from this polymerization reaction, after reverse precipitation, was 55%. The activation reaction, in which the 4-fluorophenylthio groups were oxidized to produce the linear poly(arylene ether sulfone) **P2** with activated aryl fluoride groups, was carried using H_2O_2 in formic acid (Scheme 3). The yield of **P2** was 97%.

The last step was the preparation of the dendritic polymers. We started with the synthesis of the first generation of the dendritic poly(arylene ether sulfide)s DLP1-S (Scheme 3) using **P2**, the aryl carbonate **9**, and Cs_2CO_3. The same reaction conditions used in the synthesis of polymer **P1** were employed. A minor amount of displacement of the

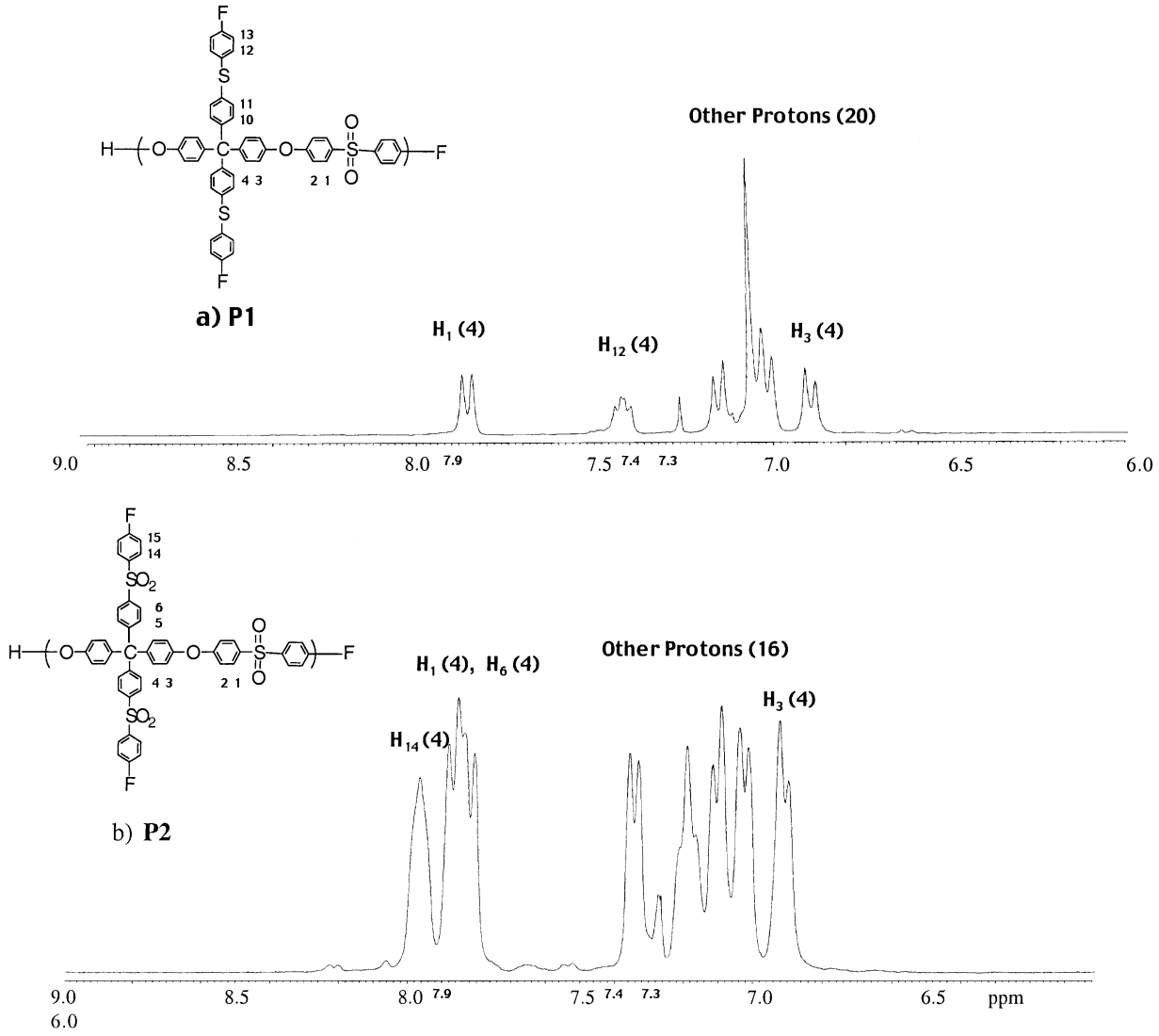


Fig. 1. ^{1}H NMR spectrum of: (a) **P1**, and (b) **P2** in $CDCl_3$ (400 MHz, 25 °C). Numbers in brackets indicate relative integration areas (Table 1).

Table 1
Characteristics of linear and dendritic poly(arylene ether)s

Product	Ideal repeat unit	FW[a] (g/mol)	H(SO_2)[b]; exp/theor	H_{12}[c]; exp/theor	H_3[d]; exp/theor	H_{Otros}; exp/theor
P1	$C_{49}H_{32}F_2O_4S_3$	819.0	4/4	4/4	4/4	20/20
P2	$C_{49}H_{32}F_2O_8S_3$	882.7	12/12	–	4/4	16/16
DLP1-S	$C_{123}H_{82}F_4O_{10}S_7$	2020.4	12/12	7/8	9/8	54/54
DLP1-SO_2	$C_{123}H_{82}F_4O_{18}S_7$	2148.4	27/28	–	8/8	47/46
DLP2-S	$C_{271}H_{182}F_8O_{22}S_{15}$	4423.3	26/28	16/16	16/16	124/122
DLP2-SO_2	$C_{271}H_{182}F_8O_{38}S_{15}$	4679.3	56/60	–	17/16	109/106
DLP3-S	$C_{567}H_{382}F_{16}O_{46}S_{31}$	9229.1	56/60	31/32	34/32	261/258
DLP3-SO_2	$C_{567}H_{382}F_{16}O_{78}S_{31}$	9741.0	121/124	–	34/32	227/226

[a] Formula weight of ideal repeated units: $FW(DLPg\text{-}S) = FW(\mathbf{P2}) + [2^g FW(\mathbf{8}) + (2^g - 2)(FW(\mathbf{8}) + 2FW(O_2)) - ((2 \times 2^g) - 2)FW(HF)]$; $FW(DLPg\text{-}SO_2) = FW(\mathbf{P2}) + [((2 \times 2^g) - 2)(FW(\mathbf{8}) + 2FW(O_2) - FW(HF))]$; where g is the generation number; $FW(\mathbf{P2}) = 882.7$ g/mol, $FW(\mathbf{8}) = 588.7$ g/mol, $FW(O_2) = 32$ g/mol, $FW(HF) = 20.01$ g/mol.

[b] Protons closer to sulfone groups: H_1, H_6, H_{14}.

[c] H_{12}: proton *ortho* to –S and *meta* to –F.

[d] H_3: proton *ortho* to –O and *meta* to the alifatic –C.

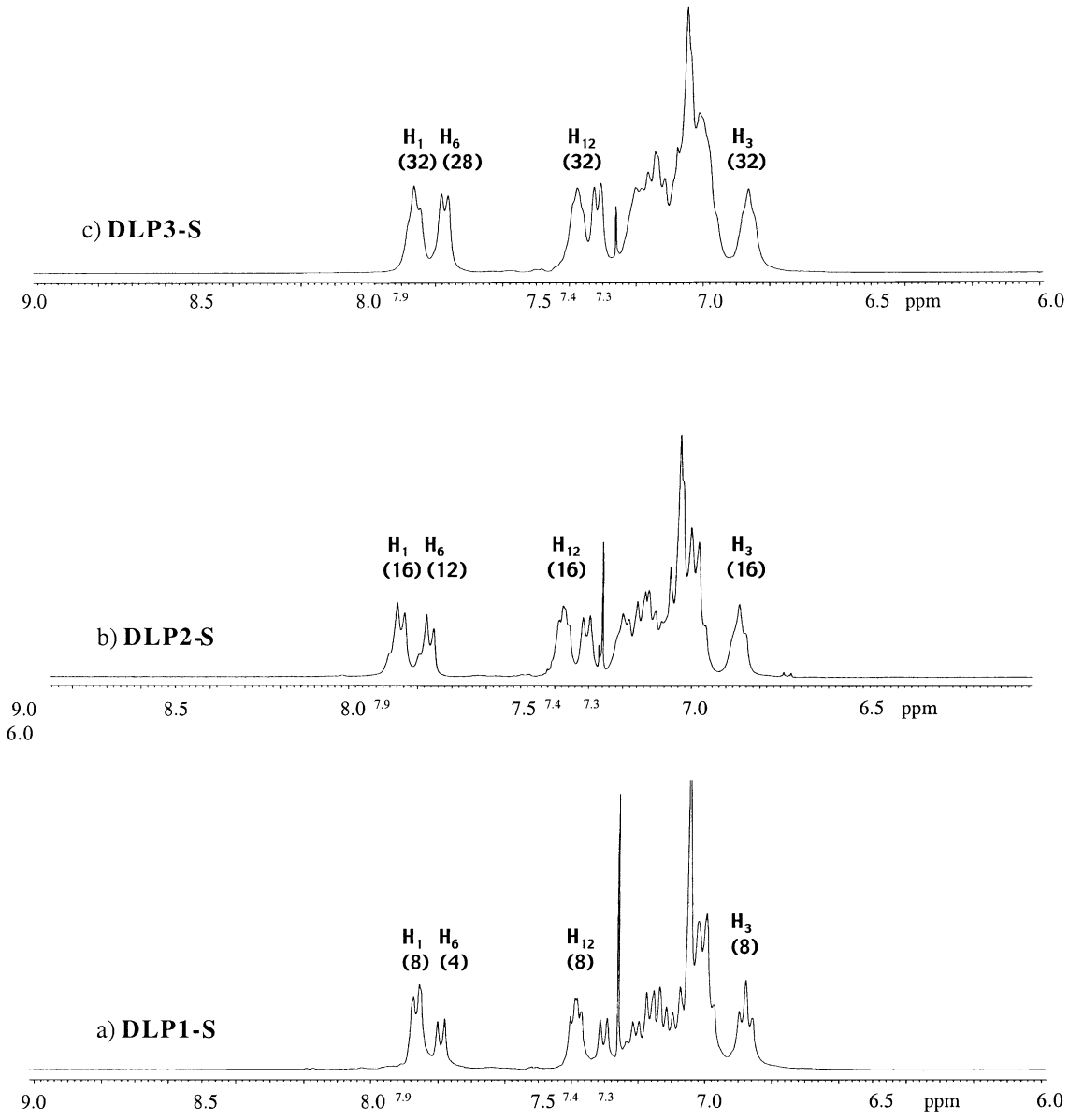


Fig. 2. ^{1}H NMR spectrum of: (a) DLP1-S, (b) DLP2-S, and (c) DLP3-S in $CDCl_3$ (400 MHz, 25 °C). Numbers in brackets indicate theoretical number of protons in the repeated unit (see Table 1 for experimental values).

unactivated fluorides is possible as described previously [16] so that the bisphenol **6** and phenol **8** could potentially self-polymerize to produce oligomers. To avoid this, the temperature of the reaction was kept around 140 °C.

The activation reaction to obtain the first generation of the dendritic poly(arylene ether sulfone)s DLP1-SO_2 was carried out under the same conditions used for the synthesis of **P2** (Scheme 3). The condensation reaction with **9** and subsequent oxidation to the sulfone was repeated to produce the second and third generations DLP2-SO_2 and DLP3-SO_2 (Scheme 4). The isolated yields of the dendritic polymers, after purification by reprecipitation of a chloroform solution of the polymers in methanol, were in the range 80–90%.

The formula weights (FWs) of the repeat units of the polymers synthesized, and the general equation used to calculate them, are given in Table 1. These values are required to calculate the amount of polymers to be used in the syntheses of DLPg-S's and to determine the isolated yield in the reactions.

3.2. NMR characterization

The synthetic strategy that we used led to two families of polymers that contained two different functionalities in the terminal units, 4-fluorophenylthio or 4-fluorophenylsulfonyl groups.

The ^{1}H NMR data are given in Section 2 and the spectra of the linear polymers and the dendritic polymers are shown in Figs. 1–3. The schematic representation of the different structural blocks that form the polymers are shown in

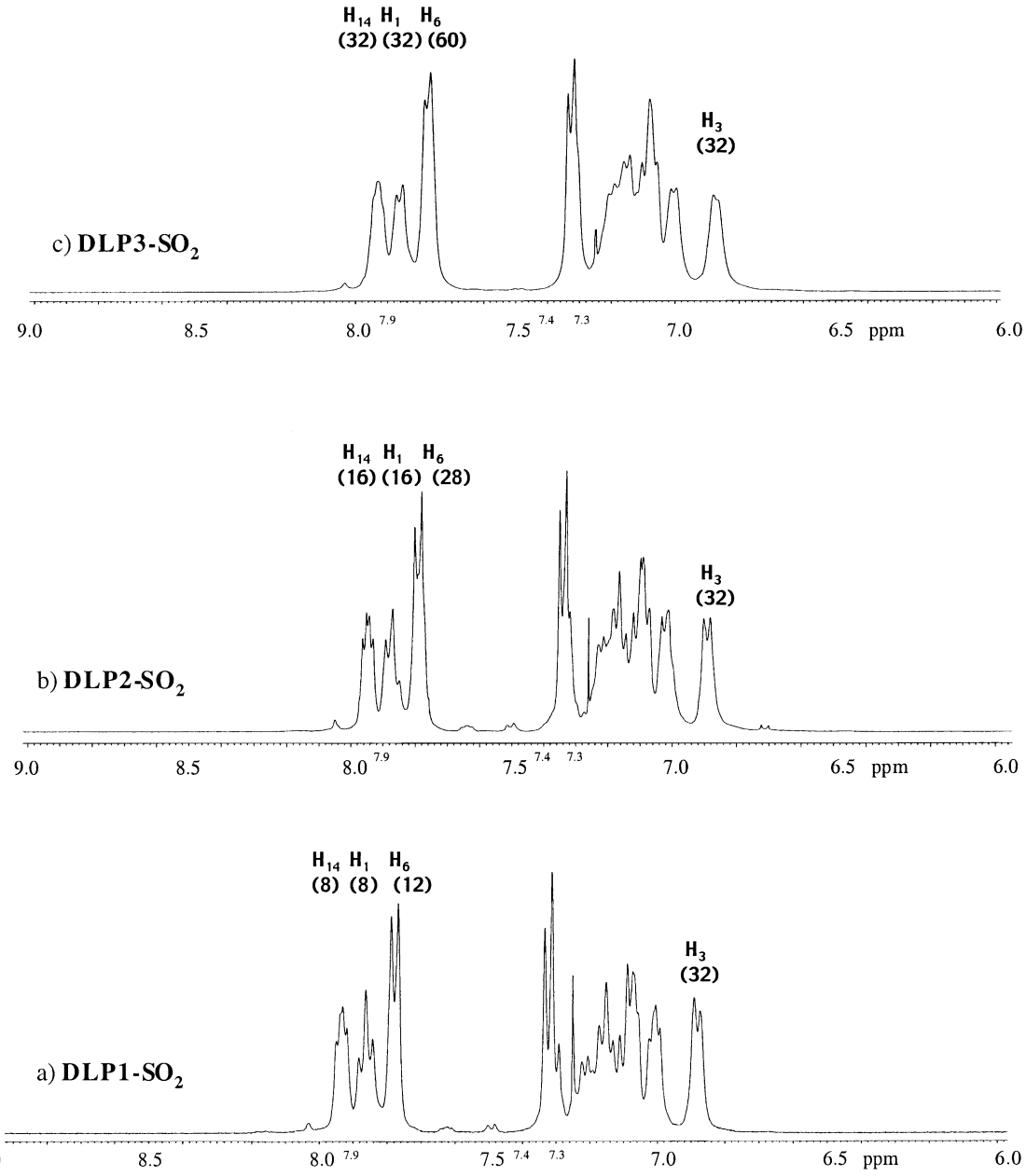


Fig. 3. ^{1}H NMR spectrum of: (a) DLP1-SO_2, (b) DLP2-SO_2, and (c) DLP3-SO_2 in $CDCl_3$ (400 MHz, 25 °C). Numbers in brackets indicate theoretical number of protons in the repeated unit (see Table 1 for experimental values).

Scheme 5. To simplify the analysis of the NMR spectra, it was assumed that all the protons identify with the same number have a similar environment, and consequently they absorb at about the same frequency.

The differences between the ^{1}H NMR spectrum of the poly(arylene ether sulfide) and the poly(arylene ether sulfone) suggest that chemical changes occurred during the oxidation and displacement reactions and that these reaction were complete. Before the displacement reaction, the starting materials **P2**, DLP1-SO_2, DLP2-SO_2, DLP3-SO_2 show a signal at $\delta = 8.0$–7.9 ppm due to the protons *ortho* to $-SO_2-$ and *meta* to –F (H_{14}, Figs. 1(b) and 3). However, after the displacement reaction the spectra of the products **P1**, DLP1-S, DLP2-S and DLP3-S (Figs. 1(a) and 3) do not show any absorbance in that area. This suggests that these reactions were almost complete since it indicates that there are no longer any protons *ortho* to $-SO_2-$ and *meta* to –F groups. If the reactions were incomplete, we should see a signal around $\delta = 7.96$ ppm due to protons H_{14}.

We can also see some important changes in the area around $\delta = 7.5$–7.3 ppm. Before the displacement reaction, there is an intense absorption at $\delta = 7.30$–7.35 ppm in the spectra of the starting materials (Figs. 1(b) and 3). After the displacement reaction, the spectra of the products show only a medium intensity broad signal at $\delta = 7.35$–7.45 ppm (H_{12}, Figs. 1(a) and 2), that can be assigned to

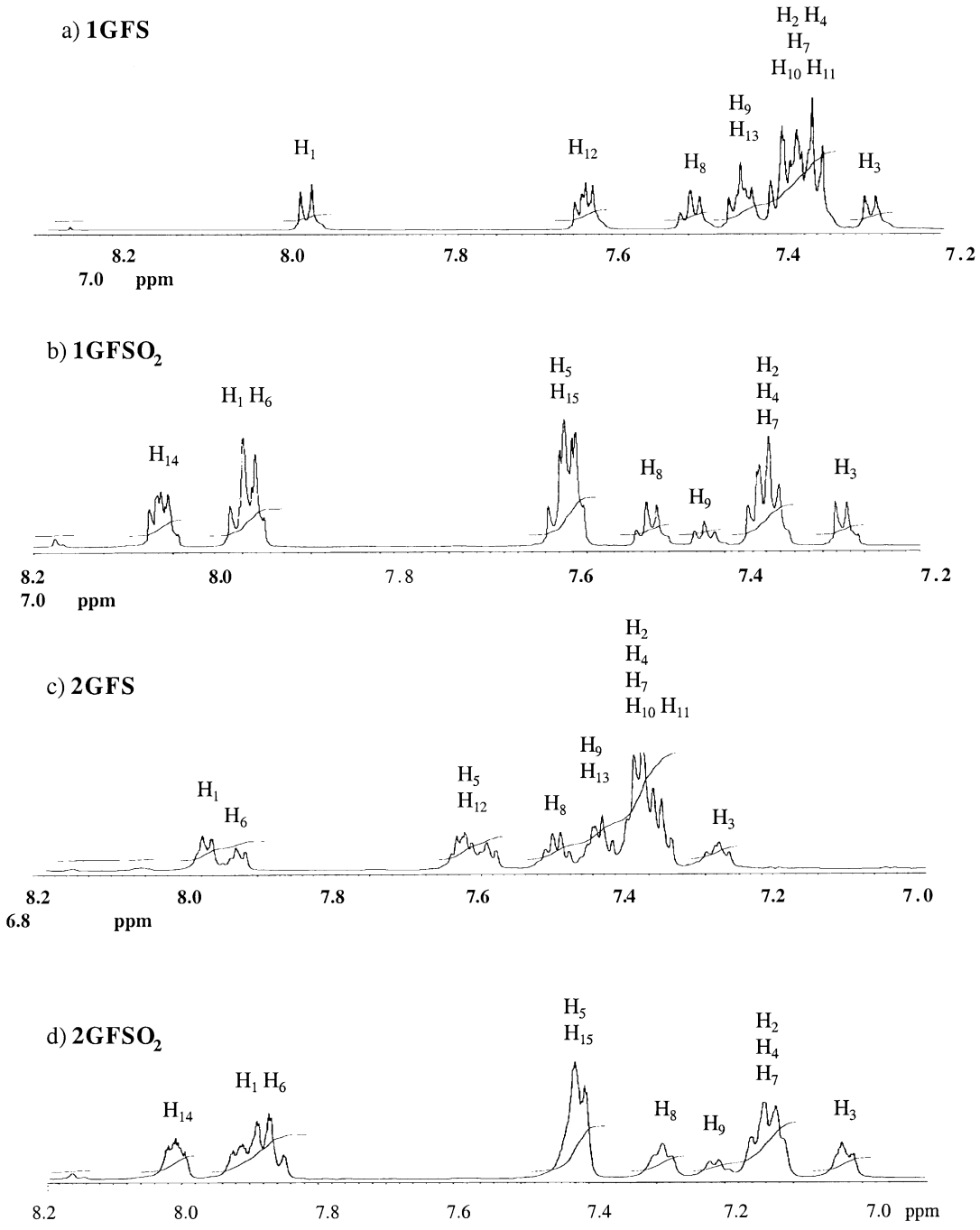


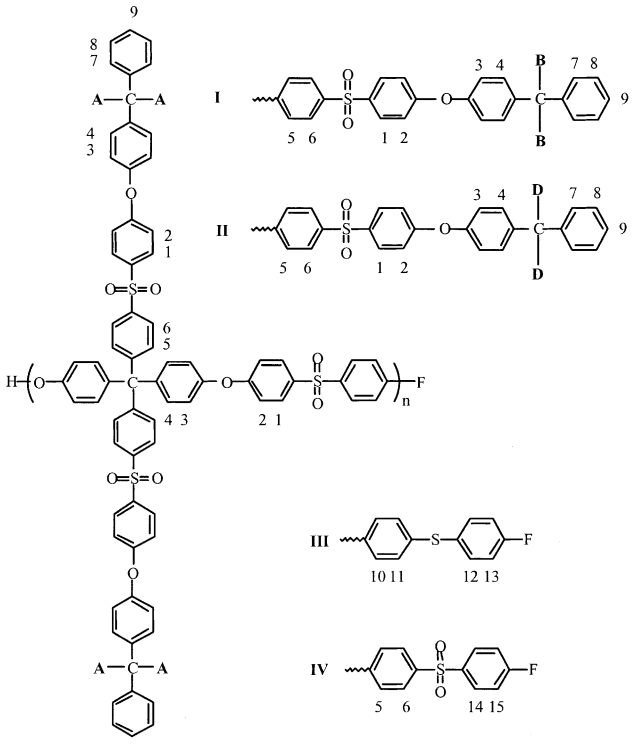
Fig. 4. ^{1}H NMR spectrum of poly(aryl ether) dendrimers [3]: (a) 1GFS, (b) 1GFSO$_2$, (c) 2GFS, and (d) 2GFSO$_2$ in $CDCl_3$ (500 MHz, 25 °C).

protons *ortho* to –S– and *meta* to –F at the terminal units of **P1**, DLP1-S, DLP2-S and DLP3-S.

The experimental values (Section 2) for the number of hydrogens adjacent to the sulfone groups (H_1, H_6 and H_{14}), and those for the protons *ortho* to the oxygen and *meta* to the aliphatic carbon (H_3), and *ortho* to –S– and *meta* to –F (H_{12}), are in good agreement with the corresponding theoretical numbers (Table 1). This fact also confirms that both reactions were essentially quantitative.

The ^{13}C NMR results also suggest that these reactions were complete. For example, before the oxidation reaction atoms C* (see Section 2 and Scheme 6), close to the sulfide group, absorb at $\delta = 135$ ppm; after the oxidation reaction this signal disappears and a new signal appears at $\delta = 131$ ppm, which corresponds to the same carbons that are now close to the sulfone groups.

The NMR information we obtained during the syntheses of the poly(aryl ether) dendrimers reported in Ref. [16] (Fig. 4) is very similar to that obtained in the present work since we used the same structural segments to build



Where:

DLP1-S: A = III

DLP2-S: A = I, B = III

DLP3-S: A = I, B = II, D = III

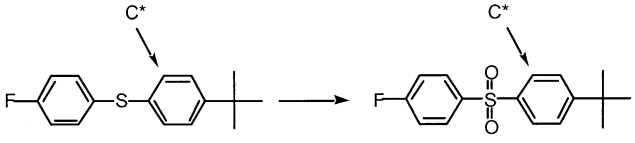
DLP1-SO$_2$: A = IV

DLP2-SO$_2$: A = I, B = IV

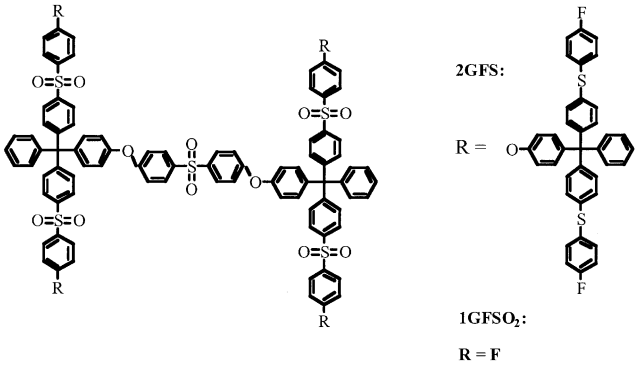
DLP3-SO$_2$: A = I, B = II, E = I V

Scheme 5.

these molecules. An example of the structures of the dendrimers is shown in Scheme 7. The ^{1}H NMR spectra of product 1GFSO$_2$ (Fig. 4(b)) shows a signal around $\delta = 8.0$ ppm which disappears almost completely after the displacement reaction (Fig. 4(c)). The absorption at $\delta = 7.5$–7.3 ppm also changes, as we described previously. Products 1GFS and 2GFS (Fig. 4(a) and (c)) resulted from the displacement of the two –F's of bis(4-difluorophenyl)sulfone and the eight –F's present in 1GFSO$_2$ (Fig. 4(b)); consequently, they have similar ^{1}H NMR spectra with no signals around $\delta = 8.0$ ppm. The respective oxidation products of 1GFS and 2GFS are 1GFSO$_2$ and 2GFSO$_2$; the last two have similar ^{1}H NMR spectra and they both show signals around $\delta = 8.0$ ppm. The relative integration areas were also in good agreement with the corresponding theoretical numbers. All of these results suggested that the reactions were complete. Although we do not give here the spectra of



Scheme 6.



Scheme 7.

the third and fourth generations the changes in the spectra were very similar (for more details, see Ref. [16]).

It should be pointed out that the identification of some protons (see area $\delta = 7.0$–7.3 ppm) was more difficult in the present work than in the case of the dendrimers obtained in Ref. [16] where peaks of the spectra are better defined. However, the most important changes in the spectra (Figs. 1–3) were observed and they could be compared with those obtained previously (Fig. 4).

As mentioned in Section 1, MALDI analyses could not be carried out because of the high molecular weight and polydispersity of these polymers. We have used the same synthetic protocol as used for the dendrimers. NMR results reported in Ref. [16] and the structures were confirmed by MALDI (no signals for partially reacted dendrimers were obtained in the corresponding products (Fig. 5 of Ref. [16])). We, therefore, believe that the MALDI results for the dendrimers adds credibility to our NMR results for the present materials.

3.3. SEC characterization and physical properties

SEC characterization and physical property data for the polymers are given in Table 2. The dendritic polymers have high values of M_n and relatively narrow polydispersity indices (PD < 1.6) similar to those of the core polymer. No increase in the polydispersity is observed in the higher generations. The molecular weights as measured by SEC do not change as they would be expected to increase considering the FW increases of the repeat units. Although FW of a generation is approximately twice the FW of the previous generation, we did not observe significant changes between different generations by SEC. We have no evidence to indicate any chain cleavage reactions, therefore we conclude that these results indicate a decrease in the hydrodynamic volume as the large bulky side groups are introduced in the polymer backbone. We were not able to obtain molecular weight values for the third generation polymers since the polymers are very strongly adsorbed on the columns. The adsorption on the columns appeared to be permanent since the concomitant pressure increase in the chromatograph

Table 2
Properties of linear and dendritic poly(arylene ether)s

Product	T_g[a] (°C)	T_d[a] 5% weight loss (°C)	η_{inh}[b] (dl/g)	M_n[c] $\times 10^{-3}$ (g/mol)	PD[c]	FW_i/FW_{P1}[d] vs. $M_{n_i}/M_{n_{P1}}$
P1	172	514	0.39	58.4	1.5	1.0/1.0
P2	241	519	0.36	45.7	1.6	1.1/0.8
DLP1-S	185	505	0.40	68.5	1.4	2.5/1.2
DLP1-SO_2	230	517	0.42	76.9	1.5	2.6/1.3
DLP2-S	187	505	0.39	71.6	1.4	5.4/1.2
DLP2-SO_2	235	513	0.40	57.2	1.5	5.7/1.1
DLP3-S	184	510	0.26	–[e]	–[e]	11.3/–
DLP3-SO_2	238	520	0.29	–[e]	–[e]	11.9/–

[a] 20 °C/min.
[b] NMP, 0.5 g/dl, 25 °C.
[c] SEC: $CHCl_3$, 1 ml/min, error ≤ 10%.
[d] Formula weight of ideal repeated units: $FW(DLPg\text{-}S) = FW(\mathbf{P2}) + [2^g FW(\mathbf{8}) + (2^g - 2)(FW(\mathbf{8}) + 2FW(O_2)) - ((2 \times 2^g) - 2)FW(HF)]$; $FW(DLPg\text{-}SO_2) = FW(\mathbf{P2}) + [((2 \times 2^g) - 2)(FW(\mathbf{8}) + 2FW(O_2) - FW(HF))]$; where g is the generation number; $FW(\mathbf{P2}) = 882.7$ g/mol, $FW(\mathbf{8}) = 588.7$ g/mol, $FW(O_2) = 32$ g/mol, $FW(HF) = 20.01$ g/mol.
[e] Sample was strongly adsorbed on column.

decreased only slightly by passing solvent through the columns for several hours. The inherent viscosities decreased in going to generation 3. This behavior in dendrimers has been noted previously [25,26].

These polymers have excellent thermal stabilities (5% weight loss > 500 °C by TGA). The polymers with terminal sulfone groups showed higher thermal stabilities and T_g's, as expected, compared with the precursor polymers with terminal sulfide groups. Good films were obtained from **P1** and **P2** by casting from chloroform solution at room temperature. The quality of the film decreased with the number of generation; for example, the third generation dendritic polymers gave a brittle film.

4. Conclusions

We have synthesized three generation of dendritic poly (arylene ether)s with activated aryl fluoride terminal functionality. The parent linear poly(arylene ether sulfide) was prepared from bis(4-fluorophenyl)sulfone and a relatively high molecular weight bisphenol containing two pendent 4-fluorophenylthio groups. The divergent approach was employed with an iterative procedure that involved oxidation of the aryl sulfide moieties to aryl sulfone groups, followed by a nucleophilic displacement reaction on the aryl fluoride now activated by sulfone groups. NMR characterization indicates that the proposed structures are correct and that the displacement and oxidation reactions were complete. These results were bolstered by the NMR and MALDI dendrimer information obtained in a previous paper [16]. The polymers have narrow molecular weight distributions and good thermal stability. Flexible films were obtained only from the first and second generations of the dendritic polymers. The molecular weights as measured by SEC and solution viscosities do not increase as would be expected taking into account the FW of the repeat units. The third generation material was adsorbed strongly on the SEC columns so that a molecular weight value could not be obtained. The latter materials also demonstrate an upper critical solution temperature in chloroform solvent. We will report in the next paper an attempt to obtain good physical properties in dendrimer containing polymers by the synthesis of dendritic-linear copolymers.

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