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Polymer 43 (2002) 5807–5817

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Synthesis of dendritic-linear copoly(arylene ether)s from a linear copolymer core

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Received 1 May 2002; received in revised form 24 July 2002; accepted 25 July 2002

Abstract

Three generations of dendritic-linear copoly(arylene ether)s containing aryl sulfide and aryl sulfone groups, and aryl fluoride terminal functionality, have been synthesized using the divergent approach and an activation/condensation sequence that involves oxidation of 4-fluorophenylthio groups and the displacement of the activated halide moiety by a phenolate ion. A copolymer was synthesized from a relatively high molecular weight bisphenol that contained two 4-fluorophenylthio groups, along with bisphenol-A, and reacted with bis(4-fluorophenyl) sulfone and Cs_2CO_3. This copolymer was oxidized with H_2O_2 in formic acid to obtain the linear copoly(arylene ether sulfone) with activated terminal groups. The dendrimer units were built up in a condensation/activation sequence as previously described using a phenol containing two 4-fluorophenylthio groups. All the polymeric products were obtained in relatively high yield (70–97%) and were characterized using NMR, SEC and HPLC. They showed excellent thermal properties (5% weight loss >450 °C by TGA) and narrow polydispersities (1.3–1.6), however, films made from third generation products were very brittle. © 2002 Published by Elsevier Science Ltd.

Keywords: Dendritic-linear copoly(arylene ether)s; Polyetherification reaction; Divergent approach

1. Introduction

Most of the effort on dendrimers has been directed toward the development of the methodology for the synthesis and the characterization of these materials and the area has been extensively reviewed [1–6]. Recently there have been a number of reports on the synthesis of dendrimers with polymer cores [3,7–9]. Frechet has recently reported the synthesis of a polymer core dendrimer from a polyphenol that has a very narrow molecular weight distribution and in this case he was able to use MALDI-TOF-MS (matrix-assisted laser desorption ionization time-of-flight mass spectroscopy) for the analysis [7].

We previously reported the synthesis of four generations of poly(arylene ether) dendrimers with terminal 4-fluorophenylthio- or 4-fluorophenylsulfonyl groups [10]. Bis(4-fluorophenyl) sulfone was used as the core and it was reacted with a phenol containing two 4-fluorophenylthio groups. The product was oxidized to the sulfone and this resulted in the activation of the fluoro groups toward nucleophilic substitution. The sequence was then continued. The best results were obtained using an aryl carbonate as a masked phenol in the polyetherification step. The structures were precisely defined through generation 4 using NMR along with MALDI-TOF-MS for the mass determination of the dendrimers.

We then extended this methodology to the synthesis of dendrimers with a polymer core [11]. A bisphenol containing two 4-fluorophenyl groups was synthesized and then converted to a poly(aryl ether). A similar activation/condensation sequence was then employed to synthesize the polymer core dendrimer. We had planned to convert the terminal fluoro groups of this polymer core dendron to sulfonic acids by conversion to thiol groups [12] followed by oxidation to the corresponding sulfonic acids [13]. Our objective was the synthesis of ion exchange membranes for use in fuel cells. Sulfonated poly(aryl ether)s have been found to have much shorter lifetimes than Nafion® based materials in fuel cells [14]. With the sulfonic acid groups on the periphery of the hydrophobic core we hoped to avoid the presumed chain scission that occurs in poly(aryl ether)s with the resulting loss of mechanical properties. Unfortunately, although the core polymer had excellent mechanical properties, the third generation product gave only brittle

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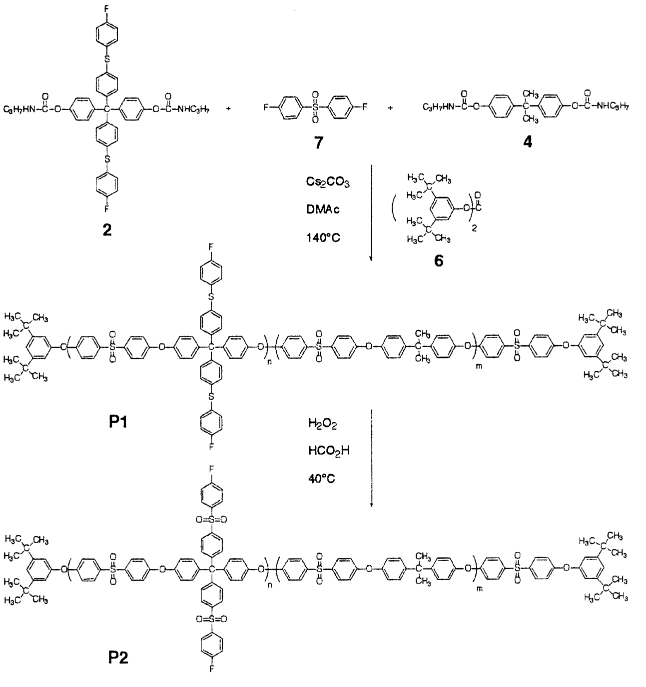
PII: S0032-3861(02)00527-X



Scheme 1.

films so that the final conversion to the sulfonic acids was not carried out.

In this paper we describe the synthesis of copolymers containing about 10% of dendrimer segments in an attempt to obtain polymer core dendrimers with good mechanical properties.

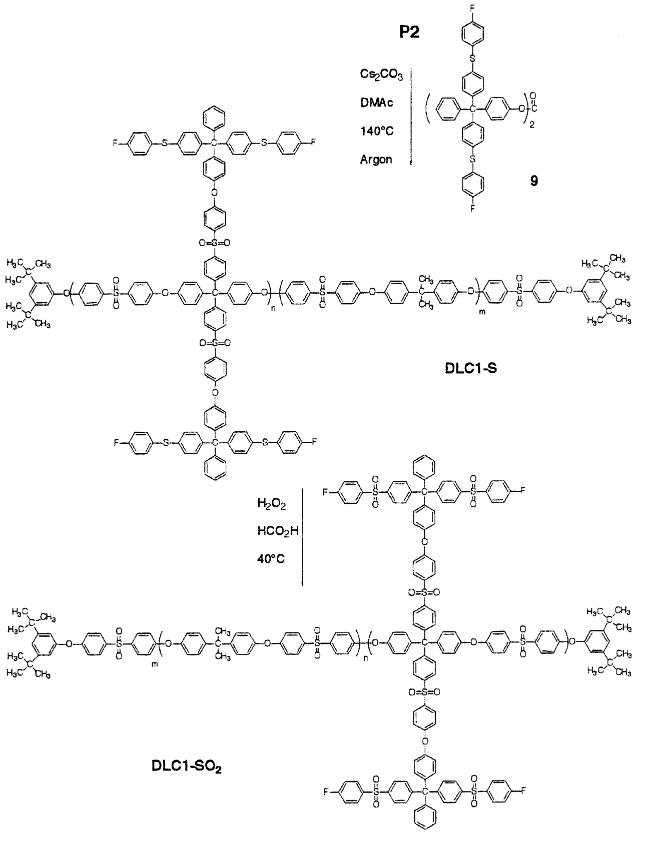
2. Experimental

2.1. Chemicals

N,*N*-dimethylacetamide (Aldrich) was dried over CaH_2 and distilled in vacuo; bisphenol-A (Aldrich), cesium carbonate (anhydrous, Aldrich), bis(4-fluorophenyl)sulfone (Aldrich), 3,5-di-*t*-butylphenol (Aldrich), formic acid 95–97% (Aldrich), hydrogen peroxide 30% (Aldrich), 1-methyl-2-pyrrolidinone (NMP, Fisher Scientific), *n*-propylisocyanate (Aldrich), triethylamine (American Chemicals Ltd), triphosgene (bis(trichloromethyl) carbonate, Aldrich), 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 (TMS) as an internal standard. 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 ultraviolet (UV) detector (Milton Roy Spectro Monitor 3100) at 254 nm, eluted by methanol at a flow rate of 1.0 ml/min. 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, eluted by chloroform ($CHCl_3$) 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 (DSC) and thermal gravimetric (TG), using a Seiko 220 instrument at a heating rate of 20 °C/min, under stream of nitrogen of 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 1-methyl-2-pyrrolidinone (NMP) at 25 °C with an #1 Ubbelohde viscometer. Efflux time of the solvent was about 160 s and the repeatability of the measurements about 5%.



Scheme 2.

2.3. Synthesis of monomers

For information about the synthesis of the products **1**, **2**

(Scheme 1), **8**, and **9** (Scheme 2) see previous reports [10, 11].

2.3.1. Aryl carbamate **4**

To a 250 ml round bottom flask fitted with a magnetic stirrer, reflux condenser, and a drying tube were added bisphenol-A **3** (4.57 g, 20 mmol), toluene (30 ml), *n*-propylisocyanate (7.50 ml, 80 mmol), and triethylamine (0.3 ml). The reaction solution was heated at 100 °C, under stirring, for 24 h. After cooling, a white solid precipitated. It was separated by filtration, washed with a small amount of toluene and petroleum ether, and dried under vacuum at 80 °C. After the workup 7.43 g of a white solid was obtained (purity of the isolated product = 98%, isolated yield = 93%). ^{1}H NMR (200 MHz, DMSO-d_6): δ 7.74–7.62 (t, 2H, –NH–), 7.22–7.10 (d, 4H, Ar, *meta* to –OCONHC$_3$H$_7$), 7.00–6.90 (d, 4H, Ar, *ortho* to –OCONHC$_3$H$_7$), 3.05–2.90 (m, 4H, –N–CH$_2$–), 1.70–1.55 (s, 6H, –C(CH$_3$)$_2$), 1.55–1.30 (m, 4H, –N–C–CH$_2$–C–), 0.95–0.75 (t, 6H, –N–C–C–CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$): δ 154.99, 149.16, 147.54, 127.91, 121.17, 43.16, 42.60, 31.21, 23.30, 11.47.

2.3.2. Aryl carbonate **6**

A mixture of 3,5-di-*t*-butylphenol **5** (10 mmol, 2.06 g), pyridine (2 ml) and toluene (10 ml) was stirred under argon for 0.5 h at 40 °C. A solution of triphosgene (2.5 mmol, 074 g) in toluene (5 ml) was added, dropwise, under the same conditions. The reaction was followed by HPLC. When the reaction was finished, it was concentrated under vacuum until a light yellow transparent viscous liquid was obtained. The viscous liquid was poured into water (50 ml) and the mixture was extracted with CHCl$_3$. The organic solution was dried with MgSO$_4$, filtered and concentrated. A white solid was recovered. It was filtered, dried under vacuum at room temperature. After the workup 1.92 g of carbonate **6** was obtained (purity of the isolated product by HPLC = 98%, isolated yield = 88%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.36–7.32 (m, 2H, Ar, *ortho* to *t*-butyl groups and *para* to carbonate group), 7.16–7.10 (m, 4H, Ar, *ortho* to *t*-butyl groups and *ortho* to carbonate group), 1.30–1.35 (s, 36H, –C(CH$_3$)$_3$); ^{13}C NMR (50 MHz, CDCl$_3$): δ 152.92, 152.68, 151.02, 120.40, 115.43, 35.28, 31.61.

2.4. Synthesis of linear copolymers

2.4.1. 10% Linear copoly(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 **2** (0.209 g, 0.270 mmol), carbamate **4** (0.965 g, 2.430 mmol), carbonate **6** (0.008 g, 0.018 mmol), anhydrous Cs$_2$CO$_3$ (0.930 g, 2.894 mmol), bis(4-fluorophenyl)sulfone **7** (0.691 g, 2.718 mmol) and DMAc (5.0 ml). The reaction mixture was stirred for 30 min under argon. The mixture was kept at 140 °C, under argon, until a very viscous solution was obtained (~20 h). Heating was accomplished with a silicone oil bath. The reaction mixture was diluted with 5–10 ml DMAc, and poured into 100 ml methanol containing a few drops of HCl. The mixture was filtered, and the separated solid was dissolved in CHCl$_3$. The solution was filtered, concentrated and the copolymer precipitated out by adding the solution, dropwise, into CH$_3$OH. The solid was collected by filtration and dried under vacuum at 80 °C (1.1 g, isolated yield = 93%). The product was purified by reverse precipitation by adding acetone (12 ml) dropwise to its solution in CHCl$_3$ (30 ml). After the separation of the copolymer P1 by decantation, it was dissolved in CHCl$_3$, precipitated in methanol and dried under vacuum at 80 °C (1.0 g, isolated yield = 77%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.90–7.80 (d, Ar, H$_1$, 16.3%), 7.46–7.38 (m, Ar, H$_{12}$, 1.5%), 7.30–7.20 (d, Ar, H$_4$, 17.2%), 7.18–6.86 (m, other aromatic protons, 40.8%), 1.74–1.64 (s, H$_{16}$, (CH$_3$)$_2$C–, 23.3%), 1.32–1.28 (s, H$_{17}$, (CH$_3$)$_3$C–, 0.8%); ^{13}C NMR (75 MHz, CDCl$_3$): δ 162.20, 161.62, 153.06, 147.41, 135.62, 135.54, 132.75, 131.73, 129.93, 128.69, 128.09, 120.05, 119.29, 118.34, 117.91, 116.97, 116.68, 42.65, 31.19.

2.4.2. 10% Linear copoly(arylene ether sulfone) P2

A typical experiment was conducted in a 25 ml round bottom flask. The copolymer P1 (0.45 g) was suspended in 18 ml of 90% formic acid with stirring. The mixture was heated to 40 °C and 1.8 g of 30% aq. hydrogen peroxide was added dropwise during 1 h. 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 copolymer P2. After the workup 0.42 g of the product was obtained (isolated yield = 92%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.00–7.92 (m, Ar, H$_{14}$, 1.7%), 7.92–7.76 (m, Ar, H$_1$ and H$_6$, 17.9%), 7.40–7.30 (d, Ar, 1.6%), 7.30–7.14 (d, Ar, 18.3%), 7.14–6.84 (2d, Ar, 35.6%), 1.74–1.64 (s, H$_{16}$, (CH$_3$)$_2$C–, 24.2%), 1.32–1.28 (s, H$_{17}$, (CH$_3$)$_3$C–, 0.7%); ^{13}C NMR (75 MHz, CDCl$_3$): δ 162.20, 154.30, 153.05, 147.41, 137.34, 135.62, 132.48, 131.73, 131.00, 129.93, 128.68, 127.48, 120.05, 119.63, 118.63, 117.90, 117.16, 42.64, 31.19.

2.5. Synthesis of dendritic-linear copolymers

2.5.1. 10% Dendritic-linear copoly(arylene ether sulfide)s

A 25 ml Pyrex three necked round-bottom flask equipped with a condenser, argon inlet–outlet, magnetic stirrer, and thermometer was charged with carbonate **9** (0.361 g, 0.300 mmol), the required starting material P2 (1.461 g, 3.000 mmol of repeated units), or DLC1-SO$_2$ (0.921 g, 1.500 mmol of repeated units), or DLC2-SO$_2$ (0.650 g, 0.750 mmol of repeated units), anhydrous Cs$_2$CO$_3$ (0.108 g, 0.330 mmol), and DMAc (16 ml/g). The reaction mixture was stirred for 30 min under argon. Then, the temperature was increased at 140 °C, and the reaction mixture was kept at this temperature, under argon, for about

18 h. Heating was accomplished with a silicone oil bath. The reaction mixture was poured, dropwise, into 100 ml methanol containing a few drops of HCl. The mixture was filtered, and the solid separated was dissolved in $CHCl_3$. The solution was filtered, concentrated and the product precipitated out by adding the solution, dropwise, into methanol. The solid was collected by filtration and purified by reverse precipitation by adding acetone dropwise to the chloroform solution. After the separation of the product by decantation, it was dissolved in $CHCl_3$, precipitated in methanol and dried under vacuum at 80 °C. The isolated yield of products was 70%.

(a) DLC1-S

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90–7.78 (m, Ar, H_1 and H_6, 16.4%), 7.44–7.36 (m, Ar, H_{12}, 2.9%), 7.34–6.86 (m, other aromatic protons, 63.0%), 1.74–1.62 (s, $(CH_3)_2C$–, 17.3%), 1.32–1.28 (s, $(CH_3)_3C$–, 0.4%); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.19, 153.04, 147.39, 144.76, 135.61, 135.37, 135.29, 132.94, 132.50, 131.85, 131.01, 129.93, 128.68, 128.13, 127.98, 120.04, 119.39, 118.60, 118.15, 117.89, 116.88, 116.67, 42.64, 31.19.

(b) DLC2-S

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.76 (m, Ar, H_1 and H_6, 16.0%), 7.44–7.36 (m, Ar, H_{12}, 4.0%), 7.36–6.84 (m, other aromatic protons, 65.2%), 1.74–1.62 (s, $(CH_3)_2C$–, 14.5%, 1.32–1.28 (s, $(CH_3)_3C$–, 0.25%); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.21, 153.06, 147.41, 144.79, 135.63, 135.37, 135.28, 132.93, 132.50, 131.87, 131.0, 129.94, 128.69, 128.17, 127.99, 120.06, 119.38, 118.66, 118.20, 117.92, 116.89, 116.67, 42.65, 31.20.

(c) DLC3-S

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.74 (m, Ar, H_1 and H_6, 15.4%), 7.44–7.36 (m, Ar, H_{12}, 4.9%), 7.36–6.82 (m, other aromatic protons, 69.6%), 1.74–1.62 (s, $(CH_3)_2C$–, 9.8%), 1.32–1.28 (s, $(CH_3)_3C$–, 0.3%); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.22, 153.06, 147.42, 144.80, 135.64, 135.38, 135.29, 132.94, 132.71, 131.88, 131.03, 129.94, 128.70, 128.17, 128.00, 120.06, 119.39, 118.49, 118.20, 117.92, 116.89, 116.68, 42.66, 31.21.

2.5.2. *10% Dendritic-linear copoly(arylene ether sulfone)s*

A typical experiment was conducted in a 25 ml round bottom flask. The required starting material DLC1-S, or DLC2-S, or DLC3-S (1.0 g) was suspended in 90% formic acid (80 ml) with stirring. The mixture was heated to 40 °C and 30% aq. hydrogen peroxide (8 g) was added dropwise. The reaction mixture was stirred for 0.5 h and the product was filtered, washed with methanol and dried at 80 °C under vacuum. The isolated yield of the products was 90%.

(a) DLC1-SO_2

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00–7.92 (m, Ar, H_{14}, m, 2.6%), 7.92–7.76 (m, Ar, H_1 and H_6, 19.1%), 7.36–6.86 (m, other aromatic protons, 60.5%), 1.74–1.62 (s, $(CH_3)_2C$–, 17.4%), 1.32–1.28 (s, $(CH_3)_3C$–, 0.4%); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.20, 153.05, 147.40, 139.94, 137.46, 135.61, 132.68, 131.84, 130.97, 130.87, 130.70, 130.48, 129.93, 128.68, 127.40, 120.05, 119.79, 118.66, 118.46, 117.90, 117.10, 116.88, 42.64, 31.19.

(b) DLC2-SO_2

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00–7.92 (m, Ar, H_{14}, 3.7%), 7.92–7.70 (m, Ar, H_1 and H_6, 19.8%), 7.40–6.80 (m, 61.3%), 1.74–1.62 (s, $(CH_3)_2C$–, 14.9%), 1.32–1.28 (s, $(CH_3)_3C$–, 0.2%); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.21, 153.05, 147.41, 139.94, 137.46, 135.61, 132.67, 131.86, 130.97, 130.88, 130.72, 130.47, 129.93, 128.69, 127.40, 120.06, 119.77, 118.66, 118.46, 117.91, 117.11, 116.88, 42.65, 31.19.

(c) DLC3-SO_2

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98–7.92 (m, Ar, H_{14}, 4.8%), 7.92–7.70 (m, Ar, H_1 and H_6, 21.4%), 7.38–6.80 (m, 64.0%), 1.74–1.62 (s, $(CH_3)_2C$–, 9.6%), 1.32–1.28 (s, $(CH_3)_3C$–, 0.2%); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.20, 153.04, 147.40, 139.92, 137.42, 135.60, 132.66, 131.85, 130.96, 130.87, 130.71, 130.46, 129.93, 128.68, 127.39, 120.05, 119.77, 118.66, 118.46, 117.90, 117.10, 116.88, 42.64, 31.19.

3. Results and discussion

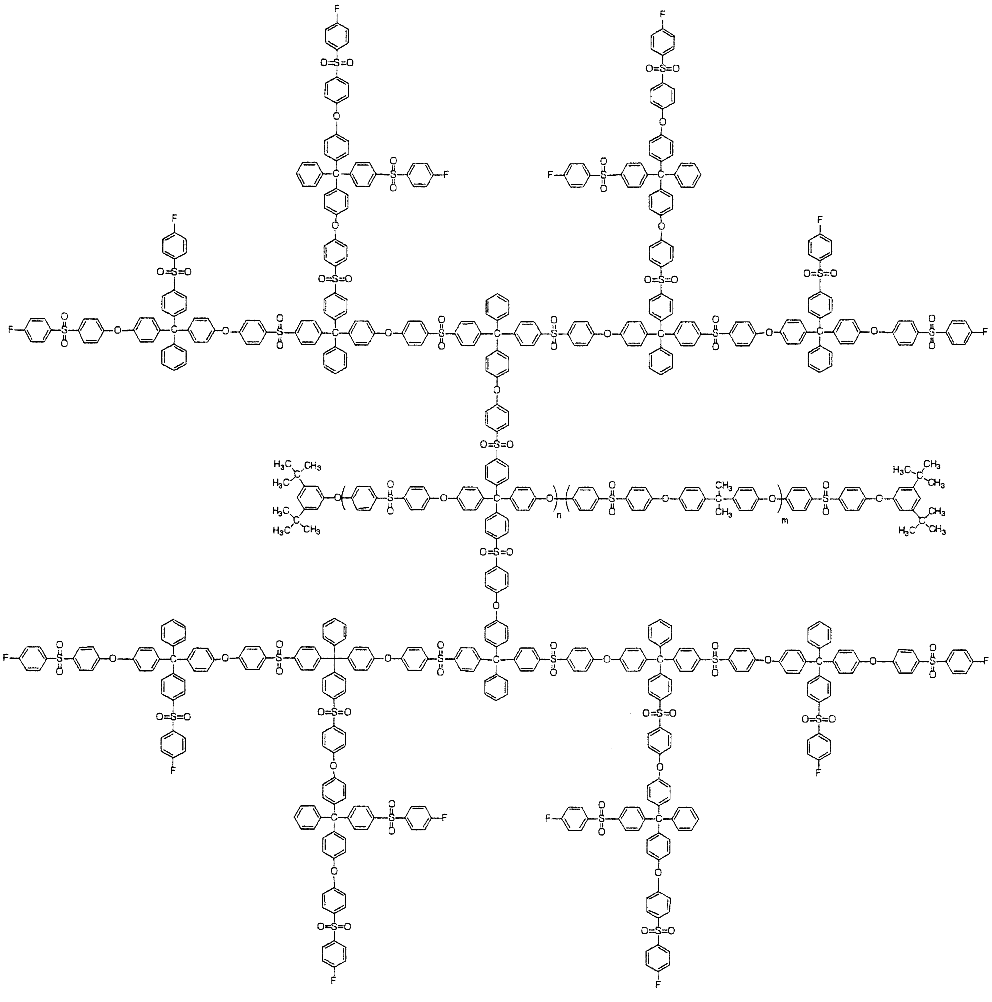
3.1. *Synthesis of monomers and polymers*

The synthesis of dendritic-linear copoly(arylene ether)s was carried out using a procedure very similar to that described in previous publications [10,11]: a divergent method based on a condensation/activation sequence. The condensation reaction is a displacement reaction of an aryl halide activated by a sulfone group reacting with a metal phenolate. The activation reaction is the oxidation of aryl sulfide moieties to produce aryl sulfone groups.

The first step of this research was the preparation of: (a) monomer **1** and its carbamate **2** [15]; (b) aryl carbamate **4** from bisphenol **3** (bisphenol-A, BPA) (isolated yield = 93%, purity by HPLC = 98%), using a procedure similar to that employed in the synthesis of **2**; (c) aryl carbonate **6** (isolated yield = 88%, purity by HPLC = 98%) from phenol **5** (3,5-di-*t*-butylphenol) employing triphosgene in pyridine/toluene at 40 °C.

We continued our work with the synthesis of the linear copoly(arylene ether sulfide) P1 and the activated linear copoly(arylene ether sulfone) P2 (Scheme 1). Copolymer P1 was prepared by reaction of the aryl carbamates **2** and **4** and the aryl carbonate **6**, with bis (4-fluorophenyl) sulfone **7** using Cs_2CO_3 as the condensation agent, and DMAc as the solvent of the reaction. The experiment was designed to get a copolymer with 10% of the unit incorporated via **2**. 3,5-Di-*t*-butylphenol **5** was used as an end-capping agent to control the molecular weight and to enable us to determine the average number of units in the copolymers using ^{1}H NMR. The isolated yield of P1, after reverse precipitation, was 77%.

The activation reaction, in which the sulfide atoms are



Scheme 3.

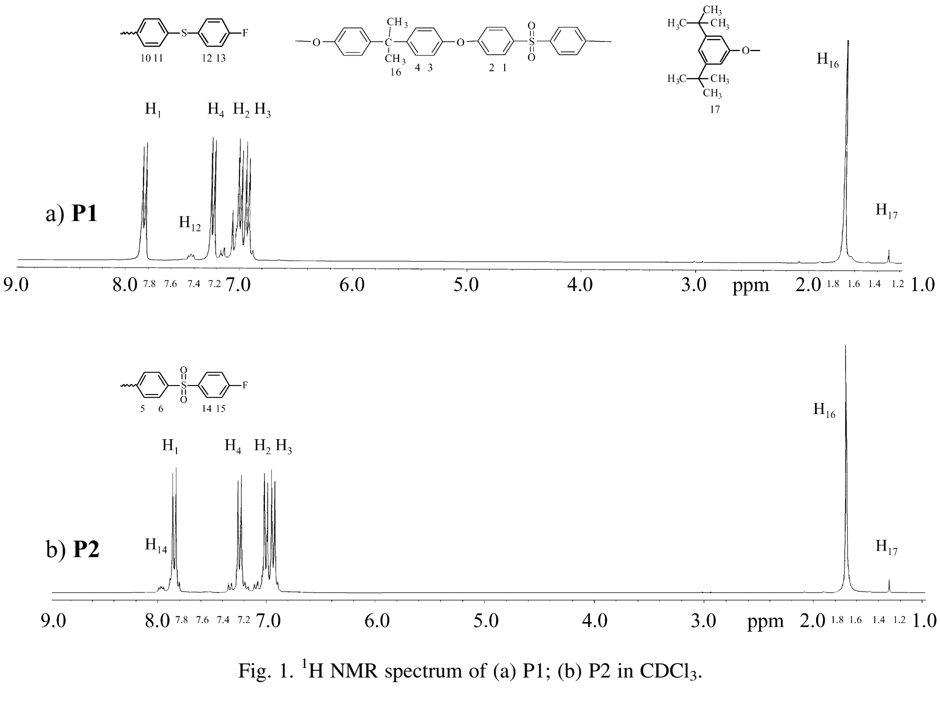


Fig. 1. ^{1}H NMR spectrum of (a) P1; (b) P2 in $CDCl_3$.

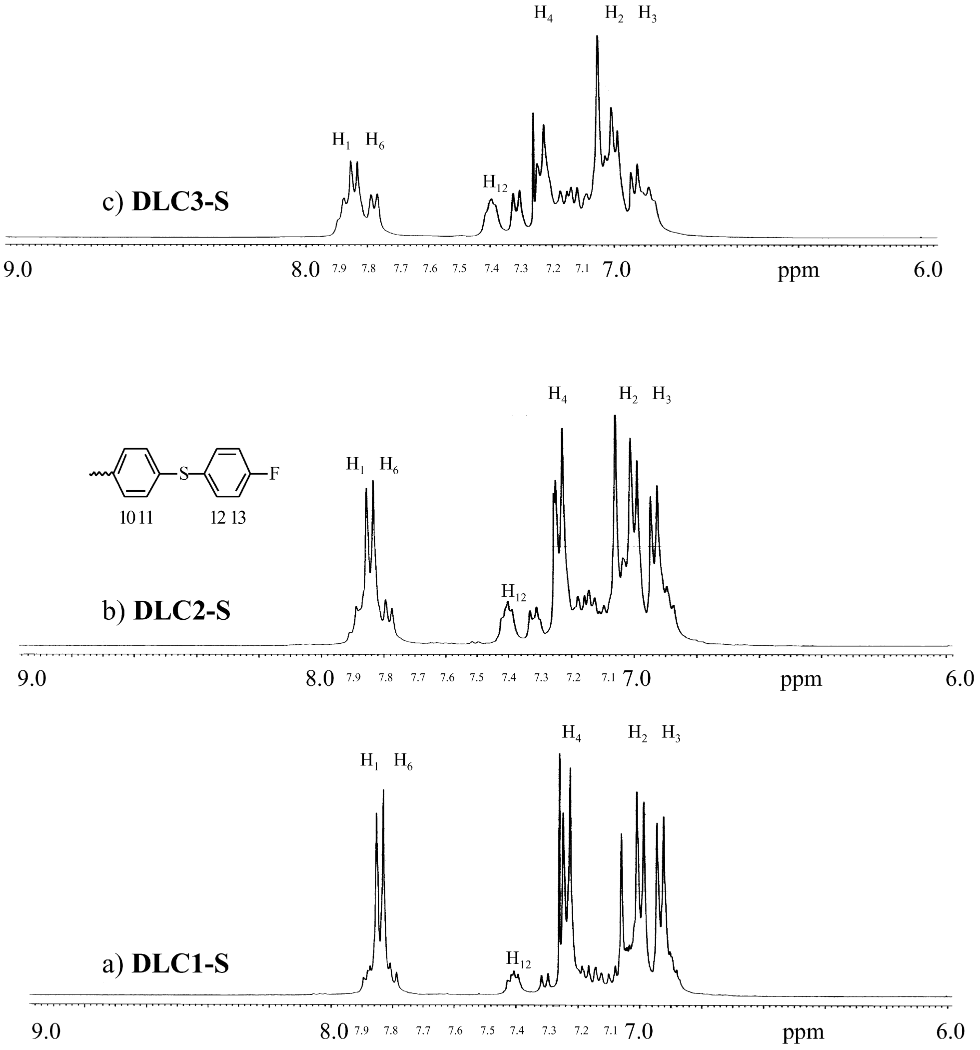


Fig. 2. ^{1}H NMR spectrum of (a) DLC1-S; (b) DLC2-S; and (c) DLC3-S. For the identification of the protons see Scheme 4.

oxidized to produce the copoly(arylene ether sulfone) P2 with activated aryl fluoride groups, was carried out using H_2O_2/HCOOH. The isolated yield of P2 was 92%.

The next step was the preparation of the dendritic-linear copoly(arylene ether sulfide)s DLC*g*-Ss and dendritic-linear copoly(arylene ether sulfone)s DLC*g*-SO_2s, where *g* represents the generation number. The synthesis of DLC*g*-Ss required the preparation of the phenol **8** and its aryl carbonate **9** [10,11].

As is shown in Scheme 2, DLC1-S was synthesized from P2, and the aryl carbonate **9** using the same reaction conditions as for the synthesis of copolymer P1. A minor amount of displacement of the unactivated fluorides is possible as described previously [10]. Therefore the bisphenol **1** 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 DLC1-SO_2 was done, using similar conditions to those employed for the synthesis of P2 (Scheme 2). The condensation/oxidation sequence was repeated to produce the second and third generation of dendritic-linear copoly(arylene ether)s (Scheme 3).

NMR characterization confirmed the proposed structure for each of these products. As mentioned in Section 1, MALDI analyses could not be carried out because of the high molecular weight and polydispersity of these copolymers. However, the dendrimer segments of the copolymer are very similar to the dendrimers [16] and dendritic-linear polymers [15] previously prepared and we used identical activation/condensation methods. The isolated yield of DLC*g*-S and DLC*g*-SO_2 were about 70 and 90%, respectively.

3.2. NMR characterization

The synthetic strategy that we used led to two families of polymers that contain two different functionalities in the terminal units of the dendritic moiety, aryl sulfide and aryl sulfone.

The ^{1}H NMR data are given in Section 2 and the spectra

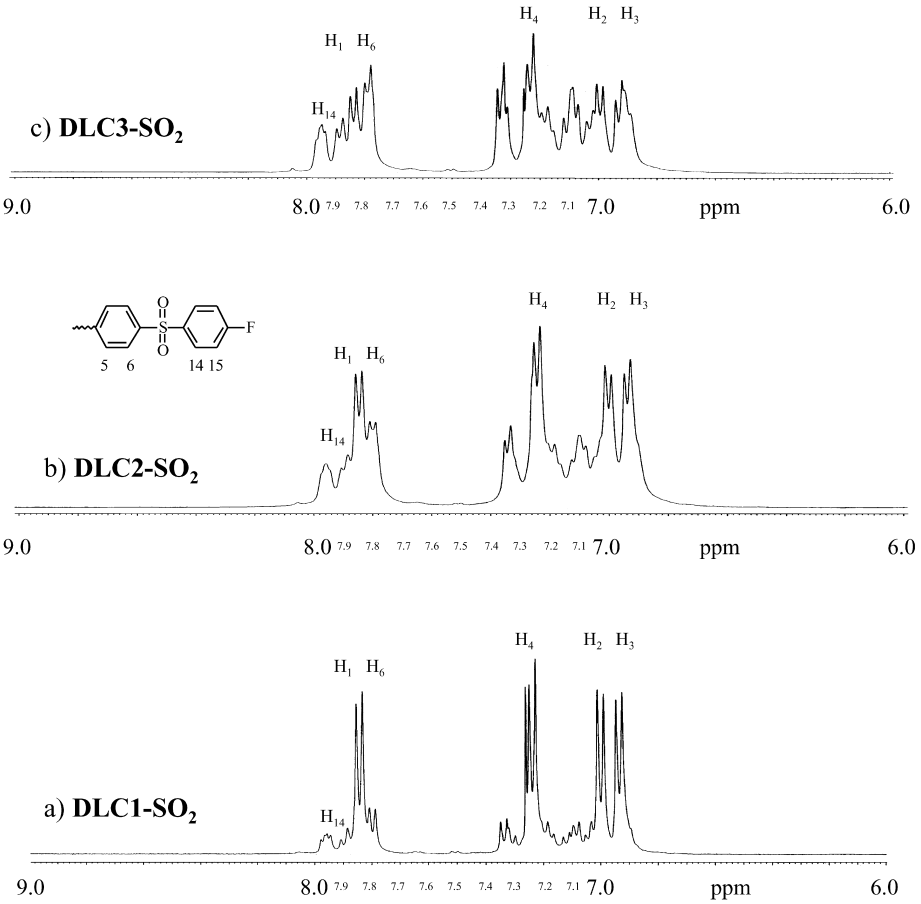


Fig. 3. ^{1}H NMR spectrum of (a) DLC1-SO_2; (b) DLC2-SO_2; and (c) DLC3-SO_2. For the identification of the protons see Scheme 4.

of the linear copolymers and the three generations of dendritic-linear copolymers are given in Figs. 1–3.

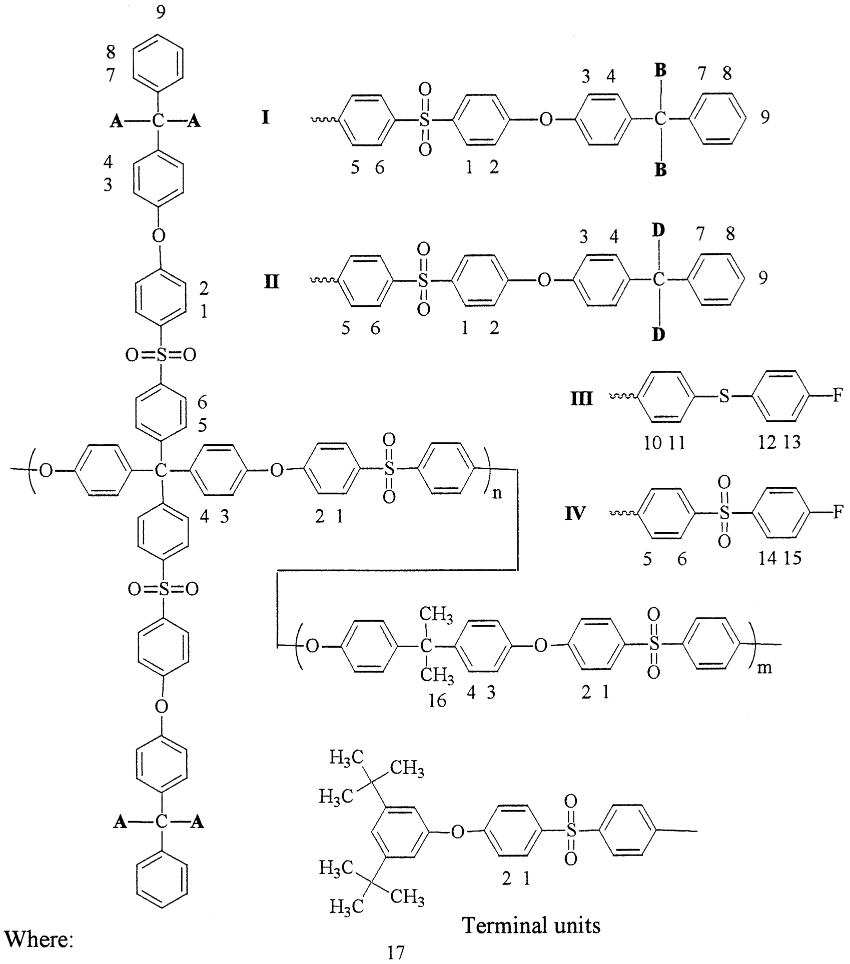
The schematic representation of the different structural blocks that form these dendritic-linear polymers and the identification of their protons are shown in Scheme 4. To simplify the analysis of the ^{1}H NMR spectra, it was assumed, that all the protons identified with the same number have a similar environment, and consequently they absorb at about the same frequency.

Examination of the spectra of the copoly(arylene ether sulfide) and the copoly(arylene ether sulfone), confirms that the proposed chemical changes occurred during the oxidation and displacement reactions and that these reactions were carried to completion. Before the displacement reaction the starting materials P2, DLC1-SO_2, DLC2-SO_2, DLC3-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. 1b and 3). However, after the displacement reaction the spectra of the products P1, DLC1-S, DLC2-S and DLC3-S (Figs. 1a and 2) do not show any absorbance in that area. That 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}.

The spectra of products P1, DLC1-S, DLC2-S and DLC3-S, show a signal at $\delta = 7.45–7.35$ ppm (H_{12}, Figs. 1a and 2) that can be assigned to protons *ortho* to $-S-$ and *meta* to $-F$ at the terminal units.

We can also observe progressive changes in the intensities of the other aromatic protons in the higher generations; e.g. the relative decrease in intensity of the aromatic protons of the linear segments, and the increase in intensities of the aromatic protons of the dendritic unit.

The NMR information we obtained during the syntheses of the poly(arylene ether) dendrimers and dendritic-linear polymers reported previously [10,11] is very similar to that obtained in the present work since we used the same structural segments to build these molecules. For example, the ^{1}H NMR spectrum of product 1GFSO_2 (first generation of the poly(arylene ether sulfone) dendrimers) shows a signal around $\delta = 8.0$ ppm which disappears almost completely in the ^{1}H NMR spectrum of 2GFS (second generation of the poly(arylene ether sulfide) dendrimers) (Fig. 4); 2GFS was generated after the displacement of the four $-$Fs present in 1GFSO_2 (Scheme 5). The same behavior was observed when we synthesized 3GFS from 2GFSO_2, or 4GFS from 3GFSO_2. The relative integration areas of the spectral lines were also in good agreement with the corresponding theoretical



Where:

DLC1-S: A = III

DLC2-S: A = I, B = III

DLC3-S: A = I, B = II, D = III

DLC1-SO_2: A = IV

DLC2-SO_2: A = I, B = IV

DLC3-SO_2: A = I, B = II, E = IV

Scheme 4.

numbers. All of these results suggested that the reactions were complete.

The ^{13}C NMR results also suggest that these reactions were complete. For example, before the oxidation reaction, the atoms of carbon closer 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 carbon atoms, now closer to the sulfone group. This result is also similar to that found for the dendrimers and the dendritic-linear polymers in our previous work.

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 previously [10] and the structures were confirmed by MALDI (no signals for partially reacted dendrimers were obtained in the corresponding products (Fig. 5 of previous paper [10]). Due to the close similarities that exist in the structures and synthetic procedures for the preparation of the poly(aryl ether) dendrimers (Scheme 5) and dendritic-linear copoly(arylene ether)s (Scheme 3), we therefore believe that the MALDI results for the dendrimers that precisely confirmed the previous structures adds credibility to our NMR results for the present materials.

From ^{1}H NMR analysis we can estimate the average number of repeat units per chain in the copolymers assuming that both ends are end-capped with 3,5-di-*t*-butylphenyl groups. For example, in the linear copoly(arylene ether sulfide) P1, the relative areas of the proton signals corresponding to the isopropylidene moiety ($6H_6$) at $\delta = 1.74$–1.64 ppm (23.3%), di-*t*-butyl group ($36H_{17}$) at $\delta = 1.32$–1.28 ppm (0.8%) and aromatic protons *meta* to –F ($4H_{12}$) at $\delta = 7.46$–7.38 ppm (1.5%), were measured. From this information we calculated the number of units generated by **4** ($m = 23.3 \times 36/0.8 \times 6 = 175$), the number

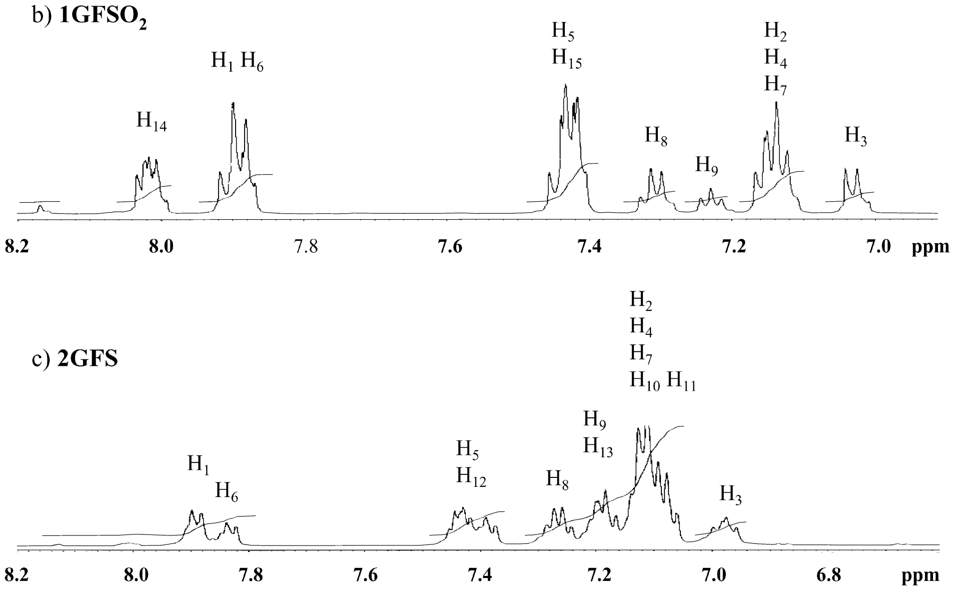
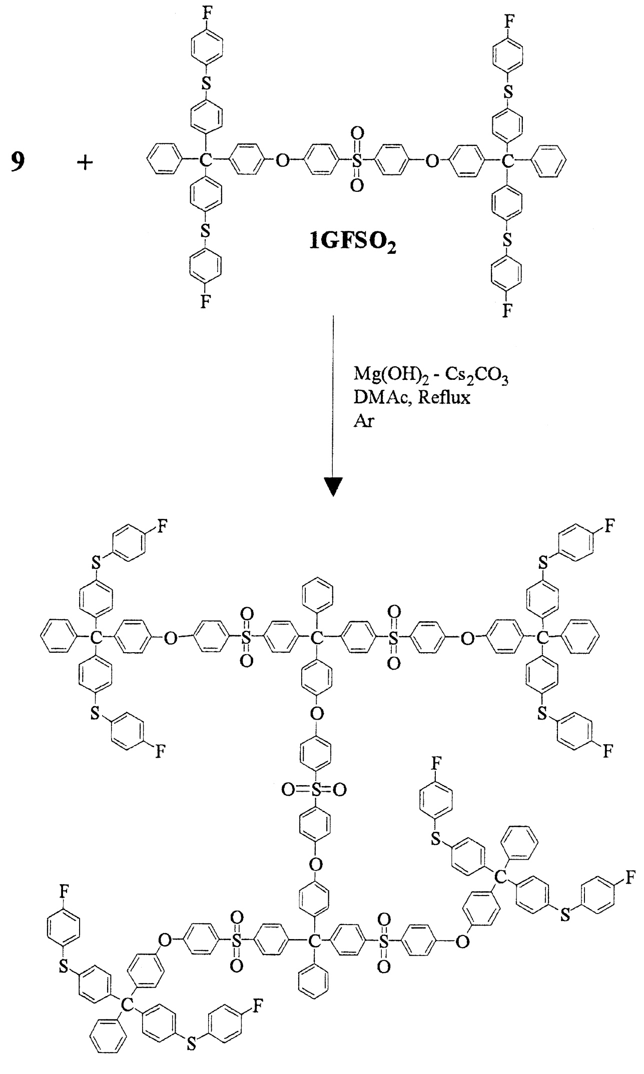


Fig. 4. ^{1}H NMR spectrum of poly(aryl ether) dendrimers [11]: (a) 1GFSO$_2$; (b) 2GFS in CDCl$_3$ (500 MHz, 25 °C).

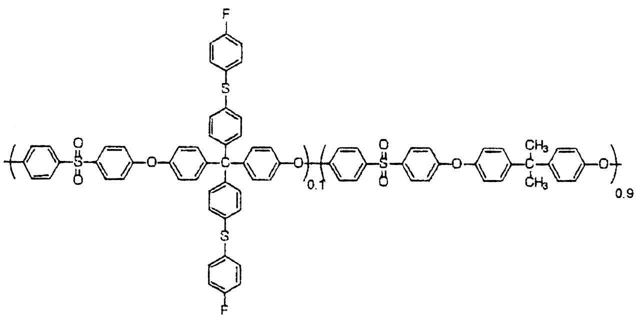


Scheme 5.

of units generated by **2** ($n = 1.5 \times 36/0.8 \times 4 = 17$), and the % of n (8.9) in the copolymer chain. To calculate the n value of generations 1, 2 and 3 the number of protons H_{12} (or H_{14}) are 8, 16 and 32, respectively. In this way, the average values of m (257), n (26), and % of n (9.2 ± 0.9) were determined. The theoretical value of n was 10% based on the amounts of **2** and **4** used. The relatively large value of the sample standard deviation of m and n ($\cong$ 20%) is a consequence of the fact that large copolymer chains were needed to get good films and consequently only very small amounts of 3,5-di-*t*-butylphenol were utilized as end-capper.

As we described previously, the structure of P1 results from the combination of two units generated by monomers **2** and **4**. Their proportions in the chain depends on the feed ratio of the monomers. Accordingly, to simplify the interpretation of the data, a hypothetical schematic representation of the repeat unit of P1 is given in Scheme 6. The repeat unit of the other polymeric products can be represented in similar way. However, we should point out that our copolymer is not a block copolymer as the hypothetical representation indicates.

In Table 1, we show the formula weight (FW) of the



Scheme 6.

Table 1
Characteristics and properties of 10% dendritic-linear copoly(arylene ether)s

Product	FW[a] (g/mol)	NHDU[b]	NH_{SO_2}[c] Exp./Theor.	T_g[d] (°C)	T_d[d] (5% wt loss; °C)	η_{inh}[e] (dl/g)	M_n[f] (10^{-3}; g/mol)	M_n[g] (10^{-3}; g/mol)	PD[g]
P1	480	32	3.8/4.0	186	518	0.56	132.5	79.1	1.3
P2	487	32	4.5/4.8	198	522	0.58	134.4	66.3	1.4
DLC1-S	601	82	4.6/4.6	187	516	0.60	165.9	74.8	1.4
DLC1-SO_2	614	82	6.1/6.4	201	518	0.59	169.5	68.7	1.4
DLC2-S	841	182	6.1/6.4	187	513	0.51	232.1	69.6	1.6
DLC2-SO_2	867	182	9.0/9.6	209	520	0.54	239.3	54.8	1.5
DLC3-S	1322	382	8.9/9.6	190	510	0.40	364.9	60.1	1.6
DLC3-SO_2	1373	382	15.2/16	223	519	0.40	379.0	49.5	1.5

[a] Formula weight (FW) of the repeated unit assuming 10% the dendritic units: $FW_{P1} = 0.9 \times FW_A + 0.1 \times FW_B$; $FW_{P2} = 0.9 \times FW_A + 0.1 \times FW_C$; $FW_{DLCg\text{-}S} = FW_{P2} + 0.1[2^g FW_{\mathbf{8}} + (2^g - 2)(FW_{\mathbf{8}} + 2FW_{02}) - ((2 \times 2^g) - 2)FW_{HF}]$; $FW_{DLCg\text{-}SO_2} = FW_{P2} + 0.1[((2 \times 2^g) - 2)(FW_{\mathbf{8}} + 2FW_{02} - FW_{HF}]$ where g is the generation number; $FW_A = 442.5$ g/mol (FW of the unit generated from **4** and **7**); $FW_B = 819.0$ g/mol (FW of the unit generated from **2** and **7**); $FW_C = 882.7$ g/mol (FW of the oxidized repeated unit generated from **2** and **7**); $FW_{\mathbf{8}} = 588.7$ g/mol, $FW_{02} = 32$ g/mol, $FW_{HF} = 20.01$ g/mol.

[b] NHDU: Number of protons present in the dendritic unit.

[c] NH_{SO_2}: number of protons closer to the sulfone groups.

[d] 20 °C/min.

[e] NMP, 0.5 g/dl, 25 °C.

[f] ^{1}H NMR: $CDCl_3$, $M_n = FW \times 283$, $m + n = 283$, error ≅ 20%.

[g] SEC: $CHCl_3$, 1 ml/min, error ≤ 10%.

repeat units of each polymeric product and the equation used to calculate them, taking into account the feed ratio of the monomers. These values are required in the experimental work to calculate the amount of polymer to be used in the syntheses of DLC*g*-Ss and the yield of the reactions.

Using the area integration data of the ^{1}H NMR spectra (see Section 2) and assuming that the total number of hydrogen atoms in the repeat unit of each polymer is given for the following equation: [(0.1 × Number of protons present in the dendritic unit) + (0.9 × Number of protons present in the unit generate by **4**)] (see Table 1 and Scheme 6), it is possible to calculate the experimental value of the number of hydrogens closer to the sulfone groups ($NH_{SO_2} = H_1 + H_6 + H_{14}$) in the repeat units of all these polymers. In all the cases, the number of protons present in the unit generated by **4** is 22. As we can see in Table 1, these values are in good agreement with the corresponding theoretical numbers.

3.3. SEC characterization

SEC characterization data is given in Table 1. Even though the polydispersities (PD) of the DLC*g*s tend to be higher than those of the linear copolymers P1 and P2, all of them showed narrow chromatographic peaks (PD < 1.6).

The Mns obtained by SEC, and based on polystyrene standards, for the linear copolymers and dendritic-linear copolymers do not change as they would be expected to increase considering the formula weight (FW) increases of the repeated units (second column, Table 1). The small changes in molecular weight observed for successive generations are probably a consequence of the small changes in polydispersity along with the changes in shape and solubility as the large bulky side groups are introduced on the polymer backbone, which could cause a decrease in the hydrodynamic volume and hence give unrealistic values by SEC. We have no ^{1}H NMR evidence to indicate any chain cleavage or incomplete reactions.

The molecular weights calculated from the ^{1}H NMR spectra are higher than those obtained by SEC and the changes are more in line with the expected results.

3.4. Physical properties

The physical properties of these new products are listed in Table 1. We observe that the T_gs of the copoly(arylene ether sulfone)s are higher than those of the copoly(arylene ether sulfide)s, probably due to their more polar and more rigid structures, and that the T_gs of the copoly(arylene ether sulfone)s tend to increase with the increase of their molecular weights and sulfone content. For example, the T_g of P2 (198 °C) is smaller than the T_g of DLC3-SO_2 (223 °C). There is little change in the T_gs of the sulfides P1 to DLC3-S.

We also observed that the inherent viscosity, η_{inh}, tends to decrease with increasing formula weight. For example, the η_{inh} of DLC1-S (0.60 dl/g) is higher than the η_{inh} of DLC3-S (0.40 dl/g) despite the fact that the molecular weight obtained by ^{1}H NMR is approximately doubled. The changes in the chemical structure could cause some changes in the polymer–solvent interactions, which could affect the hydrodynamic volume of the copolymers. This behavior in dendrimers has been noted previously [17,18].

All of these polymers were soluble in $CHCl_3$ and DMAc at room temperature and have high thermal stability as indicated by TGA (5% weight loss = 510–522 °C). Good films were obtained from P1, P2, DLC1-S, and DLC1-SO_2, by casting from chloroform solution at room temperature. However, the quality of the films obtained from the other dendritic-linear copolymers decreased with the increase of the molecular weight: the films obtained from the second generation materials were qualitatively less flexible than those obtained from the first generation and the third generation material gave a brittle film.

4. Conclusions

We have synthesized three generations of dendritic-linear copoly(arylene ether)s with activated aryl fluoride terminal functionality. For the preparation of the parent linear poly(arylene ether sulfide) and the dendritic-linear copolymers we used bis(4-fluorophenyl) sulfone, bisphenol-A and some relatively high molecular weight bisphenols synthesized previously. The divergent approach was employed with an iterative procedure that involved oxidation of the aryl sulfide moieties to aryl sulfone groups, followed by the displacement of the aryl fluoride activated by sulfone groups.

NMR characterization confirmed the proposed structures and indicated that the displacement and oxidation reactions were complete. Correlation with the NMR and MALDI analyses of the dendrimers obtained in previous work [10,11] confirmed these conclusions. The average numbers of dendritic units in the polymer chains, estimated from ^{1}H NMR spectra (9.2%), was close to the theoretical value (10%). All these polymers showed a narrow molecular weight distribution and a high thermal stability. Good films were obtained only from the linear copolymers and the first generations of the dendritic-linear copolymers.

Acknowledgements

We are grateful to Universidad de Carabobo (Venezuela) and the Natural Sciences and Engineering Research Council of Canada for financial support.

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