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SYNTHESIS OF HYPERBRANCHED OLIGOMERS WITH ACTIVATED ARYL CHLORIDE AND PHENOL TERMINAL GROUPS

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ABSTRACT

We have carried out the synthesis of hyperbranched oligomers with activated aryl chloride and phenol terminal functionality from relatively high molecular weight monomers. The syntheses have the displacement of chlorides activated by sulfone groups using phenolate ions in common. In these methods, the phenolate ion can undergo self condensation to give aryl chloride-terminated or phenol-terminated hyperbranched oligomers. The syntheses of the monomers and reactive oligomers are easily carried out and produce the products in high yield. The products were characterized by HPLC, MALDI-TOF-MS, NMR, and SEC.

INTRODUCTION

The divergent initiator core method [1] has been used in the synthesis of many dendrimers, such as poly(amido amine)s [2], poly(ethyleneimine)s [3], iptycenes [4], poly(alkyl ether)s [5], poly(amido alcohol)s [6], poly(amido ether)s [7], poly(aryl amine)s [8], polyphosphoniums [9], polysiloxanes [10], and polycarbosilanes [11]. Dendrimers are produced directly by proliferation divergently from a core.

A faster route to obtain highly branched polymer structures is the one-pot reaction of A_xB monomers, where x is 2 or greater. Tomalia called this approach the divergent uncontrolled method [12]. Highly branched but soluble polymers (non-crosslinked materials), with high molecular weight and broad molecular weight distributions can be obtained from these reactions [13]. The ideal dendritic structure of these molecules, assuming that all of the A functionalities react in an A_xB monomer, possesses one unreacted B functional group and n(x-1)+1 number of unreacted A functional groups at the surface of the polymer, where n is the degree of polymerization. However, it is much more likely that the polymer structure has defects that result in a number of linear instead of branched units. Several examples of this type of condensation to hyperbranched polymers have been reported. Kim [14] has prepared hyperbranched polyphenylenes, Fréchet [15] and Volt [16] have reported the synthesis of hyperbranched aromatic polyesters, Miller [17] and Fréchet [18] have synthesized hyperbranched poly(aryl ether)s, and Suzuki [19] has produced a hyperbranched polyamine. All of them used A_2B type condensations. According to Kim and Webster [20], these highly branched polymers can be used as polymer rheology control agents as well as spherical multifunctional macromonomers.

One of the methods used for the synthesis of poly(aryl ether)s involves the base mediated nucleophilic displacement of activated aromatic halides by aromatic phenols [20]. The ether bonds are formed via the displacement of the halide by the phenolate and the aryl halide is activated toward nucleophilic attack by an electron withdrawing group. The phenolates can be formed by reacting the phenol with stoichiometric amounts of aqueous NaOH in dimethylsulfoxide, followed by careful removal of the water as an azeotrope with chlorobenzene. An alternate route uses anhydrous K_2CO_3 as the condensation agent in an aprotic dipolar solvent such as N,N-dimethylacetamide [21]. Compared to the DMSO/aqueous NaOH system, this process appears to be nearly 10 times slower; however, a modest excess of anhydrous K_2CO_3 does not affect the polyetherification reaction. Na_2CO_3 or K_2CO_3 are commonly used and bicarbonates have also been used. Lithium carbonate is reported to have low reactivity, while rubidium carbonate and cesium carbonate, which are very effective, are less preferable for price reasons. Combinations of metal carbonates have also been used [22]. Recently, Miller [23] reported the synthesis of hyperbranched poly(aryl ether)s from a preformed sodium phenolate using NaH. This last method has the advantage that there is no formation of water in the reaction mixture, hence, the dehydration step is eliminated.

In this research, we describe the synthesis of hyperbranched oligomers with aryl chloride or phenol terminal functionality. These compounds, which have a high thermal stability, have been prepared using new monomers in a one-pot reaction. We also report herein, the synthesis of a tetrafunctional aryl chloride-terminated Generation = 0 dendrimer using, as the monomer, one of the intermediates in the synthesis of the monomer employed in the generation of the aryl chloride-terminated reactive oligomer.

EXPERIMENTAL

Materials

In experiments requiring dry solvent, N-methylpyrrolidinone, NMP (Aldrich),and DMAc (Aldrich), were dried over calcium hydride and distilled under vacuum; ethyl ether (BDH), was dried over sodium and distilled under N_2. Bis(4-fluorophenyl)sulfone (Lancaster) was recrystallized from toluene. Acetic anhydride (BDH), acetone (BDH), alumina (Aldrich), anhydrous K_2CO_3 (Omega), anhydrous $MgSO_4$ (Omega), $CHCl_3$ (BDH), 4-chlorothiophenol (Aldrich), 4,4'-dichlorobenzophenone (Aldrich), ethanol (BDH), ethyl acetate (BDH), 4-fluoroacetophenone (Aldrich), hexanes (BDH), hydrochloric acid (Caledon), mercaptoacetic acid (Aldrich), methanol (BDH), Oxone (Aldrich), phenol (A&C), phenyl magnesium bromide (Aldrich), pyridine (BDH), NaH (Aldrich), NaOH (ACS), silica gel 60 (EM), H_2SO_4 (BDH), and toluene (BDH) were used as obtained.

General Methods

^1H and ^{13}C NMR spectra were recorded as a $CDCl_3$ or a DMSO solution on Varian XL-200 and 500 MHz instruments, and chemical shifts are given in parts per billion downfield from tetramethyl silane as internal standard. Conventional mass spectra were recorded on KRATOS MS 25 RFA and DuPont 21-492B spectrometers with the ion sources operating at 200°C and 250°C, respectively, and with an impact energy of 70 eV, direct inlet: m/z (assignment). MALDI mass spectrometric analyses were performed on a Kratos Kompact MALDI III in reflectron high power mode at a wavelength of 337 nm. Dithranol was the matrix and trifluoroacetic acid the stabilizer for the system. The solutions of sample A (5 mg/mL) and matrix B (10 mg/mL) were in $CHCl_3$. The solution of the stabilizer C was in THF (2.5 mg/mL). The sample to analyze was prepared using 40 µl of A, 200 µl of B, and 20 µl of C. Melting points were determined on a Fisher-Johns

melting point apparatus and are uncorrected. HPLC analyses were carried out with a Milton Roy CM4000 instrument with auto injector using methanol as the mobile phase, a Lichrosphere 5 RP18e column (250mm x 4 mm), and UV detector (Milton Roy Spectro Monitor 3100) at a wavelength of 254 nm. Elemental analyses were performed by Galbraith Laboratories Inc.

Characterization of the Hyperbranched Oligomers and Generation = 0 Dendrimer

Inherent viscosities were measured in a calibrated number one Ubbelohde viscometer at a concentration of 0.5 g/dL in NMP at 25°C. Efflux time of the solvent was about 145 sec and the repeatability of the measurements was about 5%. Polymer molecular weights were determined relative to polystyrene standards by size exclusion chromatography, SEC, in $CHCl_3$ as the solvent on a Waters 510 HPLC with a set of four 5 μ columns (300 mm x 8 mm) arranged in series: one linear column (50 Å - 10^6 Å) and three Phenogel columns (500 Å). A UV detector was used at wavelength of 254 nm. The repeatability was lower than 10%. Differential scanning calorimetry, DSC, and thermogravimetric analyses, TGA, were performed with Seiko 220 instruments under N_2 at a heating rate of 10°C/min with gas flows of 160 mL/min 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. The repeatability was about 2°C.

Synthesis of the Generation = 0 Dendrimer

4,4'-Bis(4-chlorophenylthio)diphenyl Ketone III

A mixture of 4,4'-dichlorobenzophenone **I** (25.11 g, 0.1 mol), 4-chlorothiophenol **II** (36.16 g, 0.25 mol), anhydrous K_2CO_3 (20.73 g, 0.15 mol), and DMAc (500-mL) was mechanically stirred under N_2 for 0.5 hours at room temperature. Then, the temperature was increased to 70°C and the components were allowed to react for 12 hours. When the reaction was finished (elimination of the starting materials according to HPLC analyses), the reaction mixture was poured into 1500-mL of water and filtered. The solid obtained was washed with water, poured into 1000-mL of acetone, and boiled for 0.5 hours. The mixture was filtered and the solid obtained dried overnight under vacuum at 80°C. After the workup, 44.88 g of **III** was obtained (yield = 96%, purity of the isolated product by HPLC = 97%): m.p. 202-203°; ^1H NMR (200 MHz, DMSO-d_6) δ 7.71-7.63 (d, 4.9H), 7.55-7.51 (s, 6.7H), 7.35-7.28 (d, 4.4H); IR ($CDCl_3$) 962.8, 1013.2, 1087.6, 1180.8, 1286.3, 1311.6, 1396.2, 1475.7, 1552.3, 1589.0, 1652.5 cm-1; MS (EI) m/e Calcd. for $C_{25}H_{16}S_2Cl_2O$: 466.00196, Found 466.00196; 466, 323, 247,

184, 152, 108, 76; Analysis Calcd. for $C_{25}H_{16}S_2Cl_2O$: C, 64.24%; H, 3.45%; S, 13.72%; Found: C, 64.04%; H, 3.47%; S, 13.84%.

4,4'-Bis(4-chlorophenylthio)triphenylcarbinol V

Previously dried product **III** (23.37 g, 50 mmol), and sodium-dried ether (600-mL) were placed into a 1000-mL flask, fitted with a magnetic stirrer, a Claisen adapter with a rubber stopper and an efficient double surface condenser with a N_2 inlet. The apparatus was arranged so that the flask could be heated with a hot plate, and the ethyl ether could be distilled into the 1000-mL flask previously charged with product **III**. The reaction mixture was placed under N_2 for 0.5 hours and the phenyl magnesium bromide **IV** (3M solution in ethyl ether, 20-mL 60 mmol) was then introduced, in two fractions separated by 0.5 hours, through the rubber stopper with a syringe. When the reaction was finished (elimination of the starting material **III** according to HPLC analyses), approximately 2.5 hours later, the reaction mixture was cooled and poured into a 30% aqueous H_2SO_4 solution (600-mL) to dissolve the magnesium hydroxide. The ethereal phase was separated and dried with anhydrous $MgSO_4$. The solution was filtered and the ether evaporated under vacuum. A green-yellow viscous liquid was separated and used in this form in the synthesis of **VII**. After the workup, 22.91 g of **V** was obtained (yield = 84%, purity of the isolated product by HPLC = 85%). **V** can be purified by chromatographic column using hexane:ethyl acetate (8.5:1.5 in volume) and silica gel 60 (0.040 mm-0.063 mm): ^1H NMR (200 MHz, DMSO-d_6) δ 7.45-7.10 (m, 21H), 6.64 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 146.3, 145.6, 135.2, 133.8 (d), 133.1, 130.2, 129.8, 129.1, 128.5, 128.1, 128.0, 82.4; MS (EI) m/e Calcd. for $C_{31}H_{22}S_2C_{12}O$: 544.04891, Found 544.04891; 544, 528, 467, 385, 325, 296, 247, 241, 220, 184, 165, 152, 144, 108, 105, 77.

4-[4,4'-Bis(4-chlorophenylthio)]triphenylmethyl Phenol VII

Phenol **VI** (94.11 g, 1.00 mol), **V** (21.82 g, 0.04 mol) and a catalytic amount of H_2SO_4 were placed in a 1000-mL flask equipped with a condenser at 75°C. The mixture was allowed to react for 24 hours. When the reaction finished (elimination of starting material **V** according to HPLC analyses), water (500-mL) was added and the reaction mixture was stirred for 30 minutes. The water phase was separated and the organic phase (a viscous liquid) was diluted with ethyl ether and extracted with 20% aqueous NaOH until the color faded in the aqueous phase. Then, the ethereal phase was washed several times with water, dried with anhydrous $MgSO_4$, filtered, and the ether was evaporated under vacuum. The resulting brown

viscous liquid (purity by HPLC = 84%) was purified using flash chromatography, 5 g of sample, on a 12 cm x 5 cm column with silica gel 60 (0.040 mm-0.063 mm) using hexane:ethyl acetate (8.5:1.5 in volume) as eluent. After the workup, 16.67 g of **VII** (purity of the isolated product by HPLC = 97%) was obtained. The yield of the reaction after purification was 62%: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.33-7.06 (m, 21H), 7.06-6.97 (d, J = 8.8 Hz, 2H), 6.75-6.65 (d, J = 8.8 Hz, 2H), 5.50 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 154.3, 146.8, 146.4, 138.8, 134.1, 133.9, 133.7, 133.3, 132.7, 132.4, 131.4, 129.9, 128.2, 126.7, 115.0, 64.2; MS (EI) m/e Calcd. for $C_{37}H_{26}S_2Cl_2O$: 620.08021, Found 620.08021; 620, 543, 527, 477, 401, 257, 238, 228, 215, 181, 165, 152, 144, 108, 77; MS (MALDI(Ag)) m/e 731.9 (MI).

Product ***IX***

The sodium salt was prepared by treating **VII** (24.87 g, 0.04 mol) in ethyl ether (1000-mL) with excess of NaH (1.92 g, 0.08 mol). The solution was filtered to remove the excess NaH. The ether was removed in vacuum to obtain 24.97 g of the sodium salt of **VII** (yield = 97%, purity of the isolated product by HPLC = 96%). To a 250-mL round-bottomed flask, fitted with a condenser and a N_2 inlet, was added bis(4-fluorophenyl)sulfone **VIII** (1.271g, 5.00 mmol), the sodium salt of **VII** (7.08 g, 11.00 mmol by HPLC) and DMAc (110-mL). The mixture was stirred vigorously, maintained under reflux, and allowed to react for 3 hours. When the reaction was finished (elimination of the intermediate according to the SEC analyses), the reaction mixture was cooled, poured into methanol (440-mL) and filtered. The solid recovered was dissolved in DMAc (110-mL), coagulated in 2% aqueous hydrochloric acid (440-mL), filtered, and dried overnight at 70°C under vacuum. The crude product (5.99 g, isolated yield = 82%) was purified by fractional precipitation by dissolving the sample in $CHCl_3$ (15-20 mL/g) and using methanol as the nonsolvent. After purification, the isolated yield was about 55%: ^{1}H NMR (200 MHz, DMSO-d_6/25°C) δ 7.91-7.87 (d, Calcd. 4, Found 3.6), 7.43-7.39 (d, Calcd. 8, Found 7.4), 7.36-7.32 (d, Calcd. 8, Found 7.9), 7.32-7.27 (t, Calcd. 4, Found 4.6), 7.24-7.18 (m, Calcd. 10, Found 10.0), 7.14-7.08 (m, Calcd. 20, Found 20.3), 7.04-7.01 (d, Calcd. 4, Found 4.1); ^{13}C NMR (50 MHz, $CDCl_3$) d 161.4, 153.3, 145.9, 145.4, 142.9, 136.0, 134.0, 133.9, 133.6, 133.3, 132.9, 132.1, 131.1, 130.1, 129.8, 129.7, 128.1, 126.8, 119.5, 118.5, 65.1; MS (MALD(Li)) m/e 1462.6 (MI); T_g: 102°C (10°C/min, N_2); η_{nh} = 0.06 dL/g (NMP, 0.5 g/dL, 25°C).

Product ***X***

Wet alumina was prepared by adding water (10-mL) to the alumina (50 g; Brockman grade I, 200 mesh) and shaking until a free flowing homogeneous

powder was obtained. The sulfide **IX** (4.37 g, 3.00 mmol) was added to a vigorously stirred suspension of wet alumina (12.00 g) and Oxone (22.20 g, 36.00 mmol) in $CHCl_3$ (150-mL). The mixture was refluxed and allowed to react for 24 hours. The reaction time was chosen according to the purity of the product obtained after its characterization. Then, the reaction mixture was cooled, filtered and the solids washed thoroughly with $CHCl_3$. The solution was concentrated, coagulated in methanol (300-mL), and the separated solid was dried overnight at 100°C under vacuum. After the workup, 4.61 g of **X** was obtained (isolated yield = 97 %): ^1H NMR (500 MHz, DMSO-d_6/25°C) δ 7.96-7.92 (d, Calcd. 8, Found 7.6), 7.92-7.86 (m, Calcd. 12, Found 11.5), 7.68-7.64 (d, Calcd.8, found 7.4), 7.43-7.39 (d, Calcd. 8, Found 8.3), 7.32-7.28 (t, Calcd. 4, Found 4.5), 7.24-7.19 (t, Calcd. 2, Found 2.4), 7.16-7.09 (m, Calcd. 12, Found 12.2), 7.04-7.00 (d, Calcd. 4, Found 4.2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 161.0, 153.8, 151.5, 144.4, 141.2, 140.3, 139.9, 139.6, 136.2, 132.6, 131.9, 130.8, 130.1, 130.0, 129.6, 128.6, 127.5, 127.4, 119.8, 118.7, 65.8; MS (MALDI(Li)) m/e 1589.9 (MI); T_g = 168°C (10°C/min, N_2); η_{inh} = 0.06 dL/g (NMP, 0.5 g/dL, 25°C).

Synthesis of Reactive Oligomer XIV

*Acetylated Product **XI***

To 18.65 g (30 mmol) of **VII** in pyridine (79 g, 100 mmol), acetic anhydride (102 g, 100 mol) was added, dropwise, at 0°C. The ice bath was removed and the components were allowed to react for 24 hours at room temperature. The reaction time was chosen according to the purity of the product obtained after its characterization. The contents were poured into a beaker containing 200-mL of 10-15% aqueous HCl at 0°C. A gum was obtained, which was dissolved in ethyl ether, and the solution extracted with water. The ethereal phase was separated, dried with $MgSO_4$, filtered, and evaporated on a ratavapor. The separated gum was dried under vacuum at 70°C, overnight, to yield 19.51 g of **XI** (yield = 98%, purity of the isolated product by HPLC = 99%): ^1H NMR (50 MHz, DMSO-d_6) δ7.5-7.2 (m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.1, 148.9, 146.0, 145.5, 143.7, 133.8 (d), 133.2, 132.1, 131.1, 129.7, 128.1, 126.7, 121.0, 65.1, 22.8; MS (EI) m/e Calcd. for $C_{39}H_{28}S_2Cl_2O_2$: 662.09077, Found 662.09077; 662, 585, 554, 543, 527, 477, 443, 435, 401, 257, 241, 228, 181, 165, 152, 144, 112, 97, 84; Analysis Calcd. for $C_{39}H_{28}S_2Cl_2O_2$: C, 70.58%; H, 4.25%; S, 9.66%; Cl, 10.68%; Found: C, 70.18%; H, 4.36%; S, 9.84%; Cl, 10.49%.

*Oxidation Product **XII***

The method is similar to that employed for the synthesis of **X**. Product **XI** (16.59 g, 25 mmol) was added to a vigorously stirred suspension of wet alumina

and Oxone (92.50 g, 150 mmol) in $CHCl_3$ (250-mL). The mixture was heated at reflux and allowed to react for 24 hours. The reaction was followed by TLC (aluminum sheet of silica gel 60 F_{254}, hexanes:ethyl acetate, 6:4). When the reaction was finished (elimination of intermediates of the reaction according to TLC analyses), the reaction mixture was cooled, filtered, and the solid was washed thoroughly with $CHCl_3$ and eliminated. The solution (liquid obtained after the filtration) was concentrated and coagulated in methanol (200-mL). The precipitate (15.46 g) was dissolved in 15-mL of acetone and coagulated in 30-mL of methanol to afford 10.67 g of **XII** (yield = 59%). The purity was checked by TLC: ^1H NMR (200 MHz, DMSO-d_6) δ 8.40-7.60 (m, 8H), 7.76-7.64 (d, J = 8.6 Hz, 4H), 7.50-7.40 (d, J = 8.5 Hz, 4H), 7.40-7.00 (m, 9H), 2.25 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.1, 151.6, 149.2, 144.4, 142.1, 140.3, 139.9, 139.5, 132.0, 131.9, 130.8, 130.0, 129.6, 129.5, 128.6, 127.5, 127.3, 121.6, 65.9, 22.8; Analysis Calcd. for $C_{39}H_{28}S_2Cl_2O_6$: C, 64.37%; H, 3.88%; S, 8.81%; Found: C, 64.02%; H, 3.98%; S, 9.03%.

Activated Monomer p-[4,4'-Bis(4-chlorophenylsulfonyl)triphenylmethyl Phenol ***XIII***

Ethanol (150-mL), DMAc (50-mL) and K_2CO_3 (2.76 g, 20 mmol) were added to product **XII** (14.55 g, 20 mmol) . The reaction was carried out at 100°C for 1 hour with stirring. The reaction time was chosen according to the purity of the product obtained after its characterization. Then, the reaction mixture was cooled and poured into 10% aqueous HCl. The precipitate was separated by filtration, washed with water, and dried at 100°C under reduced pressure to afford 13.15 g of a light brown solid (isolated yield = 96%). The purity of the product was checked by TLC (aluminum sheet of silica gel 60 F_{254}, hexane:ethyl acetate, 6:4): ^1H NMR (500 MHz, DMSO-d_6) δ 9.50 (s, 1H, H_{10}), 7.90-7.98 (d, 4H, H_8), 7.90-7.82 (d, 4H, H_7), 7.70-7.60 (d, 4H, H_9), 7.40-7.35 (d, 4H, H_6), 7.30-7.20 (t, 2H, H_4), 7.10-7.20 (t, 1H, H_5), 7.10-7.05 (d, 2H, H_3), 6.90-6.80 (d, J = 7.8 Hz, 2H, H_2), 6.70-6.60 (d, J = 7.8 Hz, 2H, H_1); ^{13}C NMR (50 MHz, $CDCl_3$) δ 154.9, 152.3, 144.9, 140.3, 139.8, 139.1, 136.2, 132.1, 132.0, 130.8, 130.1, 129.6, 128.5, 127.4, 127.1, 115.6 (C_2), 65.7; MS (MALDI(Ag)) m/e 795.2 (MI).

Reactive Oligomer ***XIV***

The sodium salt of **XIII** was prepared by treating **XIII** in ethyl ether with excess of NaH; the solution was filtered to removed excess NaH and the ether was removed in vacuum.

To a 25-mL round-bottomed flask, fitted with a condenser and a N_2 inlet, the sodium salt of **XIII** (1.415 g, 2 mmol) and NMP (10-mL) was added. The reaction mixture was stirred vigorously and heated. After 2 hours, the reaction mixture was cooled, poured into methanol (440-mL) acidified with a few drops of HCl, and filtered. The solid recovered was dissolved in DMAc (10-mL), the solution was filtered and coagulated in aqueous 2% HCl (40-mL). The precipitate was filtered and dried overnight at 100°C under vacuum to obtain 1.07 g of **XIV**. Assuming that all the n monomer molecules reacted and that n molecules of HCl were lost during the reaction, the isolated yield was 82%: ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.00-7.78, 7.70-7.54, 7.44-7.34, 7.34-7.18, 7.18-7.04, 7.04-6.92, 6.92-6.88; ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 161.4, 153.4, 151.4, 150.9, 144.2, 141.2, 140.0 (d), 139.5, 139.3, 134.9, 132.3, 131.5, 131.4, 130.3, 130.1, 129.6, 129.2, 128.3, 127.0 (d), 119.5 (C_1), 118.0 (C_2), 64.5; MS (MALDI(Ag)) m/e 1407.8, 2056.9, 2706.5, 3355.7, 4004.6, 4652.6, 5301.5, 5950.0; *Tg* = 226°C (10°C/min, N_2), 5% weight loss = 462°C (10°C/min, N_2), 5% weight loss = 461°C (10°C/min, O_2); η_{inh} = 0.10 dL/g (NMP, 0.5 g/dL, 25°C).

Synthesis of Reactive Oligomer XXIV

*4-(4-Chlorophenylthio)phenyl Methyl Ketone **XVII***

A mixture of 4-chlorothiophenol **XV** (47.73 g, 0.33 mol), 4-fluoro-acetophenone **XVI** (41.44 g, 0.30 mol), anhydrous K_2CO_3 (24.88 g, 0.18 mol), and DMAc (1000-mL) was mechanically stirred under argon for 0.5 hours at room temperature. After, the temperature was increased to 60°C and the components were allowed to react for 24 hours. When the reaction was finished (elimination of the starting material **XVI** according to HPLC analyses), the reaction mixture was poured into 2000-mL of water. The precipitate was filtered (isolated yield = 100%, purity of the isolated product = 95%), recrystallized from methanol:water (6:1), (15-mL CH_3OH/g), and dried to obtain 52.03 g of **XVII** (yield = 66%, purity of the isolated product by HPLC = 98%): m.p. 52-54°C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 7.96-7.84 (m, 2H), 7.60-7.42 (bs, 4H), 7.36-7.24 (m, 2H), 2.55 (s, 3H); ^{1}C NMR (50 MHz, $CDCl_3$) δ 196.5, 144.1, 135.2, 135.1, 135.0, 131.2, 130.2, 129.3, 128.1, 28.0; MS (EI) m/e Calcd. for C_{14} H_{11} S Cl 0: 262.02191, Found 262.02191; 262, 247, 184; Analysis Calcd. for C_{14} H_{11} S Cl 0: C, 64.00%; H, 4.22%; S, 12.20%; Cl, 13.49%; Found: C, 63.82%; H, 4.25%; S, 12.48%; Cl, 13.34%.

1,1,1-[4-(4-Chlorophenylthio)-4',4"-dihydroxy]triphenylethane ***XIX***

To a mixture product **XVII** (26.28 g, 0.10 mol), phenol **VI** (56.46 g, 0.60 mol), and a catalytic amount of mercaptoacetic acid ($HSCH_2COOH$) **XVIII** kept at room temperature was added 96% conc. H_2SO_4 (30.08 g). After 4 days (elimination of starting material XVII according to HPLC analyses), 400-mL of water were added to the reaction mixture (the color changed from red to blue), stirred for a few minutes, and left overnight. A white solid precipitated which was filtered, washed with water, and dried for 3 hours at 70°C under vacuum to obtain 35.94 g of **XIX** (yield = 83%, purity of the isolated product by HPLC = 93%): m.p. 156-158°C; ^1H NMR (200 MHz, DMSO-d_6) δ 7.45-7.20 (m, 6H), 7.10-7.00 (d, 2H), 6.88-6.78 (d, J = 8.7 Hz, 4H), 6.72-6.64 (d, J = 8.8 Hz, 4H), 2.55 (s, 3H); 13C NMR (50 MHz, DMSO-d_6)) δ 155.0, 149.7, 138.9, 134.7, 131.7, 130.7, 130.0, 129.6, 129.5, 129.2, 128.0, 114.8, 51.5, 31.4; MS (IE) m/e Calcd. for $C_{26}H_{21}SClO_2$: 432.09507, Found 432.09507; 432, 417, 323, 247, 195, 184, 165, 152, 144, 119, 108, 94, 77.

Acetylated Product ***XXI***

To 32.48 g (75 mmol) of **XIX** in pyridine (75 g) at 0°C was added acetic anhydride **XX** (110 g) dropwise. The ice bath was removed and components were allowed to react for 24 hours at room temperature. The contents were poured into a beaker containing 750-mL of 20% aqueous HCl at 0°C. The yellow viscous liquid separated by decantation was dissolved in ethyl ether and the solution extracted with water. The ethereal phase was separated, dried with $MgSO_4$, filtered, concentrated, and left overnight in a covered beaker. The precipitate was separated by filtration and washed with ethyl ether. After the workup, 26.37 g of **XXI** (yield = 68%, purity of the isolated product by HPLC = 98%) was obtained: m.p. 153-155°C; ^1H NMR (200 MHz, DMSO-d_6)) δ 7.50-7.25 (m, 8H), 7.14-7.06 (m, 8H), 2.27 (s, 6H), 2.14 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.3, 149.0, 148.0, 146.0, 134.4, 113.3, 132.7, 130.7, 129.9, 129.7, 121.4, 52.9, 32.1, 22.8; MS (IE) m/e Calcd. for $C_{30}H_{25}SClO_4$: 516.11620, Found 516.11620; 516, 501, 459, 417; Analysis Calcd. for $C_{30}H_{25}SClO_4$: C, 69.69%; H, 4.87%; S, 6.20%; Cl, 6.86% Found: C, 69.60%; H, 5.01%; S, 6.46%; Cl, 6.79%.

Oxidation Product ***XXII***

The method is similar to that employed for the synthesis of **X**. Product **XXI** (18.10 g, 35 mmol) was added to a vigorously stirred suspension of wet alumina (35.00 g) and Oxone (64.79 g, 105 mmol) in $CHCl_3$ (90-mL). The mixture was

heated at reflux for 8 hours. Then, the reaction mixture was cooled, filtered, and the solid washed thoroughly with $CHCl_3$. The solution was concentrated and poured into methanol (150-mL). The precipitate was separated by filtration and washed with methanol to afford 14.60 g of **XXII** (isolated yield = 76%). Sometimes it was necessary to leave the $CHCl_3$-methanol solution overnight in a covered beaker to obtain the solid. The purity of the solid was checked by TLC (aluminium sheet of silica gel 60 F_{254}, hexanes:ethyl acetate, 6:4): m.p. 167-169°C; ^1H NMR (200 MHz, DMSO-d_6) δ 8.05-7.97 (d, J = 8.7 Hz, 2H), 7.97-7.90 (d, J = 8.5 Hz, 2H), 7.75-7.65 (d, J = 8.8 Hz, 2H), 7.37-7.30 (d, J = 8.7 Hz, 2H), 7.08 (s, 8H), 2.27 (s, 6H), 2.14 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.2, 154.8, 149.2, 145.0, 140.3, 140.0, 139.2, 130.1, 129.9, 129.8, 129.5, 127.7, 121.6, 53.4, 32.0, 22.8; MS (EI) m/e Calcd. for $C_{30}H_{25}SCl0_6$: 548.10603, Found 548.10603; 548, 506, 491, 464, 449, 279, 213, 112, 43; Analysis Calcd. for $C_{30}H_{25}SCl0_6$: C, 65.63%; H, 4.59%; S, 5.84%; Cl, 6.49%; Found: C, 65.18%; H, 4.68%; S, 6.08%; Cl, 6.88%.

*Activated Monomer 1,1,1-[4-(4-chlorophenylsulfonyl)-4',4''-dihydroxy]tri-phenyl-ethane **XXIII***

To product **XXII** (5.49 g, 10 mmol) was added ethanol (75-mL) and K_2CO_3 (1.38 g, 10 mmol). The reaction mixture was stirred at 60°C, and allowed to react for 8 hours. Then, the mixture was poured into 75-mL of water and acidified slowly to pH = 2-4 using conc. HCl. A gum was formed which was separated by decantation, dissolved in ethyl ether (75-mL), and the solution washed with water, dried with $MgSO_4$, filtered and concentrated under reduced pressure. The concentrated solution was treated with petroleum ether with stirring until a solid precipitated. The beige solid was separated by filtration and dried to afford 4.42 g of **XXIII** (isolated yield = 95%). The purity was checked by TLC (aluminum sheet of silica gel 60 F_{254}, hexanes:ethyl acetate, 5:5): m.p. 228-230°C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.90-7.86 (d, J = 8.8 Hz, 2H), 7.80-7.76 (d, J = 8.8 Hz, 2H), 7.50-7.46 (d, J = 8.8 Hz, 2H), 7.24-7.20 (d, J = 8.8 Hz, 2H), 6.88-6.84 (d, J = 8.8 Hz, 4H), 6.74-6.70 (d, J = 8.8 Hz, 4H), 5.00 (s, 2H), 2.05 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 156.7, 155.7, 140.3, 139.0, 138.5, 138.2, 130.1, 129.8, 129.5, 129.4, 127.3, 115.0 (C_1), 51.3, 30.3; MS (EI) m/e Calcd. for $C_{26}H_{21}SClO_4$: 464.08490, Found 464.08490; 464, 449, 294, 279, 159, 111.

*Reactive Oligomer **XXIV***

A 25-mL, Pyrex, three-necked round-bottom flask equipped with a Dean-Stark trap filled with toluene, condenser, nitrogen inlet-outlet, magnetic stirrer, and

thermometer was charged with **XXIII** (0.581 g, 1.25 mmol), anhydrous K_2CO_3 (0.190 g, 1.375 mmol), and NMP:toluene (1:1). A monomer concentration in NMP of 0.5 mol/L was employed. N_2 was sparged through the reaction mixture with stirring for 30 minutes, and then the mixture was kept at 130°C until no further water was collected. Then, toluene was removed slowly while the reaction mixture was heated up. The bath temperature was maintained at 180-190°C for 3 hours under N_2. Heating was accomplished with a silicone oil. The reaction mixture was allowed to cool, diluted with 5-10-mL DMAc, and poured into 20-40-mL methanol containing a few drops of hydrochloric acid. The mixture was filtered, and the solid dried overnight at 100°C under vacuum. After the workup 0.42 g of product was obtained. Assuming that all the **n** monomer molecules reacted and that **n** molecules of HCl were lost during the reaction, the isolated yield was 78%: ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.10-8.90 (d), 7.96-7.70 (m), 7.36-7.18 (m), 7.18-6.86 (m), 6.86-6.72 (m), 6.72-6.60 (m), 2.40-1.90 (m); MS (MALDI(Ag)) m/e 966.1, 1394.7, 1822.9, 2251.8, 2680.1, 3109.0, 3536.2. *Tg* = 261°C (10°C/min, N_2), 5% weight loss = 395C (10°C/min, N_2); η_{inh} = 0.25 dL/g (NMP, 0.5 g/dL, 25°C).

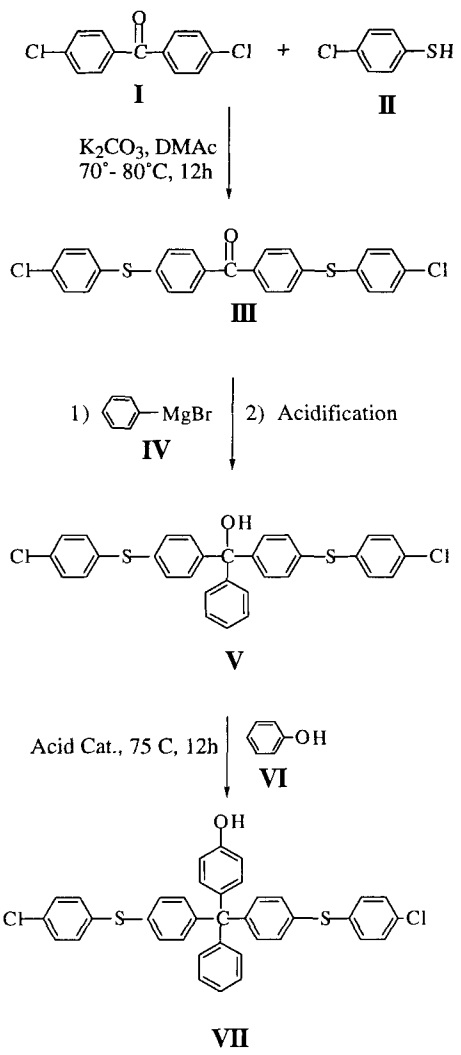
*Acetylated Oligomer **XXV***

To 0.33 g of **XXIV** in pyridine (6-mL) at 0°C acetic anhydride (6-mL) was added dropwise. The ice bath was removed and the components were allowed to react for 24 hours at room temperature. The contents were poured into a beaker containing 50-mL of 10-15% aqueous HCl at 0°C. After filtration, the solid obtained was dried at 100°C overnight under vacuum. There was obtained 0.30 g of **XXV**: ^{1}H NMR (200 MHz, DMSO-d_6) δ 8.00-7.70 (bs, H_2, H_3), 7.36-7.16 (bs, H_4), 7.16-6.80 (bs, H_1, H_6, H_7, H_9, H_{10}), 2.30-1.90 (bs, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.3, 161.5, 154.7, 153.1, 149.1, 145.1, 144.4, 139.6, 135.1, 130.4, 129.8, 129.5, 127.3, 121.7 (C_1), 120.0 (C_2), 118.3 (C_3), 52.0, 30.2, 21.1; IR ($CDCl_3$) 1014.14, 1110.49, 1153.58, 1169.22, 1208.57, 1247.22, 1295.45, 1320.15, 1500.17, 1587.40, 1753.93 cm^{-1}; MS (MALDI (Ag)) m/e 1049.2, 1520.8, 1991.0, 2461.5, 2931.9, 3402.0, 3872.6, 4343.0, 4813.0, 5283.3; *Tg* = 242°C (10°C/min, N_2), 5% weight loss = 420C (10°C/min, N_2); η_{inh} = 0.22 dL/g (NMP, 0.5 g/dL, 25°C).

RESULTS AND DISCUSSION

The initial goal of this research was to synthesize dendritic polymers with aryl chloride terminal functionality. The reagents for the monomer synthesis (**VII**)

Scheme 1



are relatively inexpensive and all the reactions are easy to carry out (Scheme 1). However, during the course of the research we realized that, using the preformed sodium phenolate, only the generation = 0 of the dendritic polymers (**IX** and **X**) could be prepared quantitatively (Scheme 2). Synthesis of the higher generations was not possible due to the low reactivity of the sodium phenolate. The same result was obtained when we tried to prepare the higher generations of aryl fluoride-

terminated dendritic polymers using a monomer with a similar general structure but possessing fluorine instead of chlorine groups [24]. The preparation of dendritic polymers involves multistep reactions, consequently it requires very high yields and high purity starting materials. Thus, we decided to use monomer **XIII**, which is the activated form of monomer **VII**, to prepare the aryl chloride-terminated reactive oligomer **XIV** (Scheme 4). To complement this work, we also prepared a bisphenol to synthesize the phenol-terminated reactive oligomer **XXIV**. The descriptions of all these syntheses are shown below.

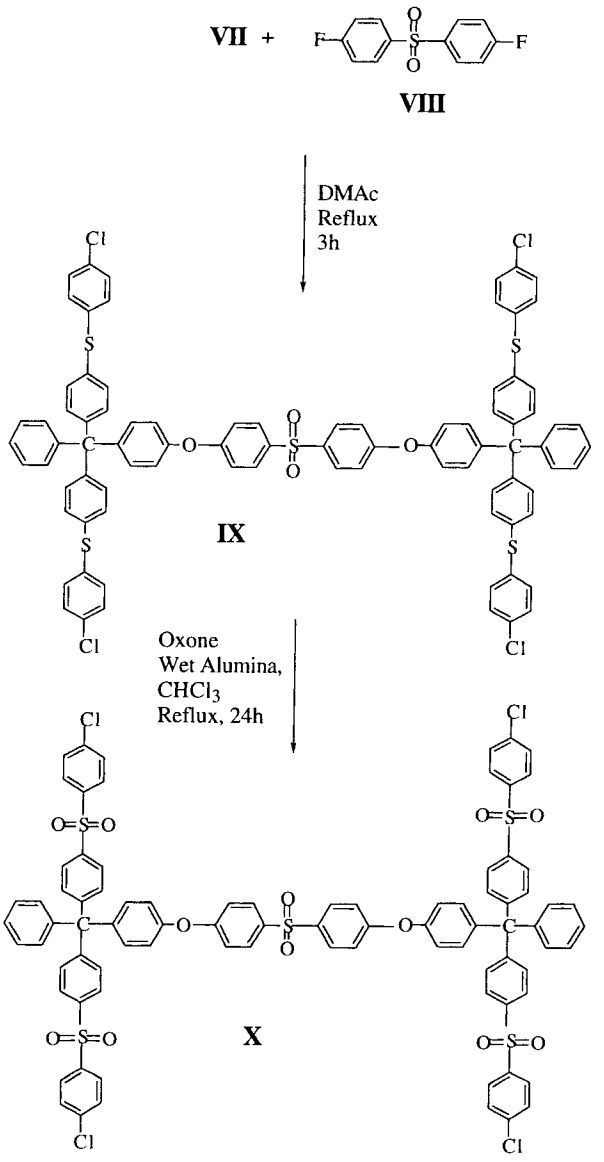
The syntheses of **X** and **XIV**, respectively, start with the preparation of phenol **VII** as shown in Scheme 1. The reaction begins with displacement of the chloride groups of 4,4'-dichlorobenzophenone **I** by two molecules of 4-chlorothiophenol **II** using K_2CO_3 under mild conditions [25] to obtain the condensation product **III**. Then, product **III** was **reacted** with phenyl magnesium bromide **IV** [26] to produce the tertiary alcohol **V**. The alcohol **V** was condensed [27] with phenol **VI** in the presence of an acid catalyst to generate the monomer **VII**. The overall yield of **VII** from 4,4'-dichlorobenzophenone **I** was 50%. NMR and MS characterization of each of those products confirmed the proposed structures (see Experimental Section). The purity of **VII**, determined by HPLC after purification on a chromatographic column, was 97%.

We carried out the synthesis of the tetrafunctional product **X** using a condensation and an oxidation reaction. The condensation is a displacement reaction of an aryl fluoride activated by a sulfone group using a preformed sodium phenolate. This method avoids the azeotropic distillation since no water is produced in this reaction. In the oxidation, the aryl sulfide moieties generate aryl sulfone groups.

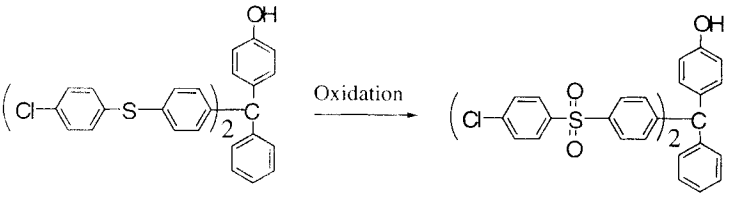
The phenolate was prepared by treating the purified phenol **VII**, with NaH in ethyl ether. The synthesis of **IX** (Scheme 2) requires reflux conditions (164°C) since the elimination of the monosubstituted product becomes difficult when a lower temperature was employed. A stoichiometric excess of the phenolate with respect to the bis(fluorophenyl) sulfone was used. The reaction yield was about 80%. The oxidation reactions, to produce compound **X** (yield = 97%), was carried out using Oxone as the oxidizing reagent [28]. The synthesis is shown in Scheme 2. The products were characterized by SEC, NMR, and MALDI-TOF-MS. Details of the characterization will be given later.

The etherification chemistry utilized in the preparation of the tetrafunctional product **IX** by the divergent approach was used for the one-pot synthesis of **XIV**. Miller [17] reported a similar procedure to synthesize hyperbranched poly(aryl

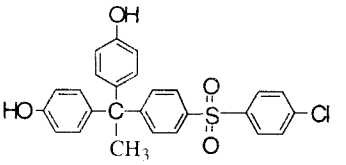
Scheme 2



Scheme 3



VII **XIII**



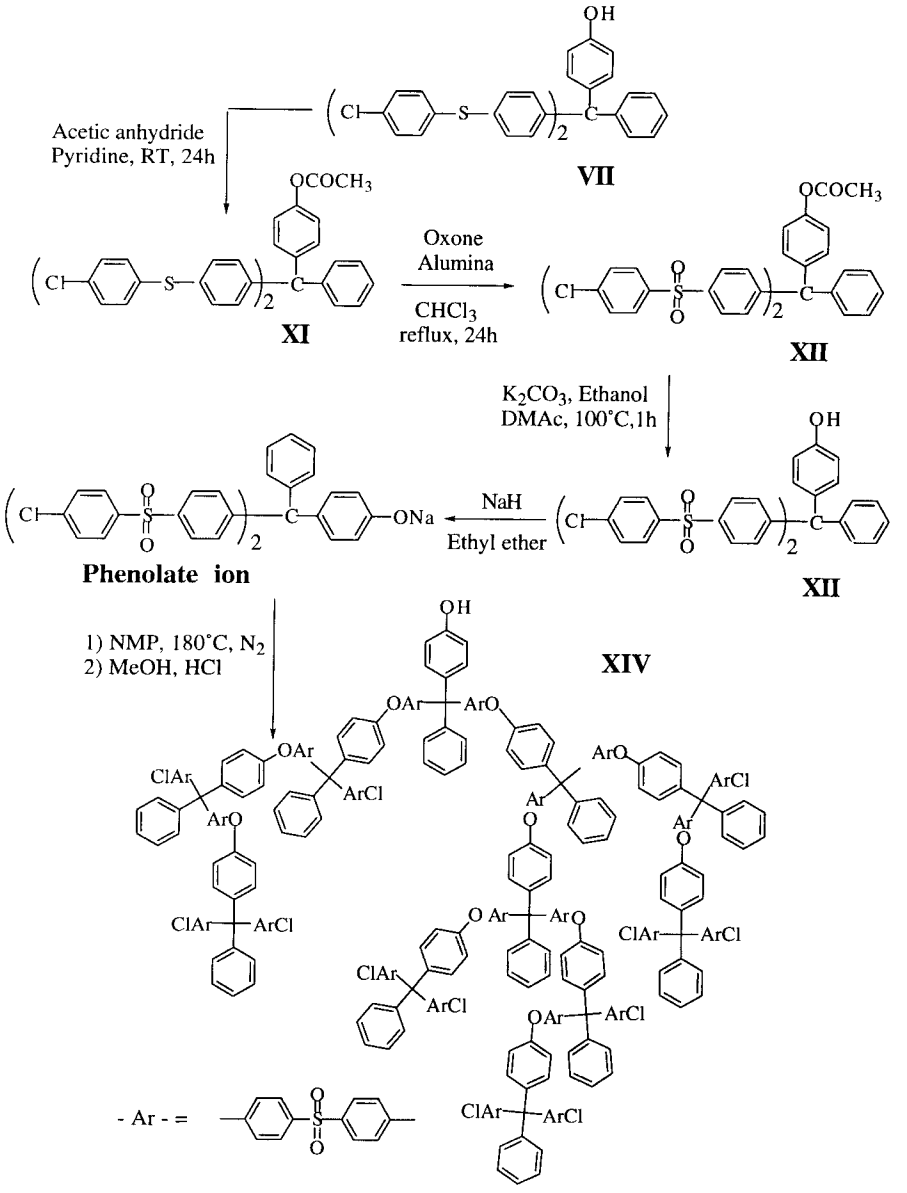
XXIII

ether)s. In the present case phenol **VII** is activated, through the oxidation of the sulfide groups to give phenol **XIII** (Scheme 3). The phenol contains a single hydroxyl group and two aryl chloride groups which are activated toward nucleophilic displacement by sulfone moieties. This relatively high molecular weight monomer can now undergo self condensation to give the aryl chloride-terminated reactive oligomer **XIV**.

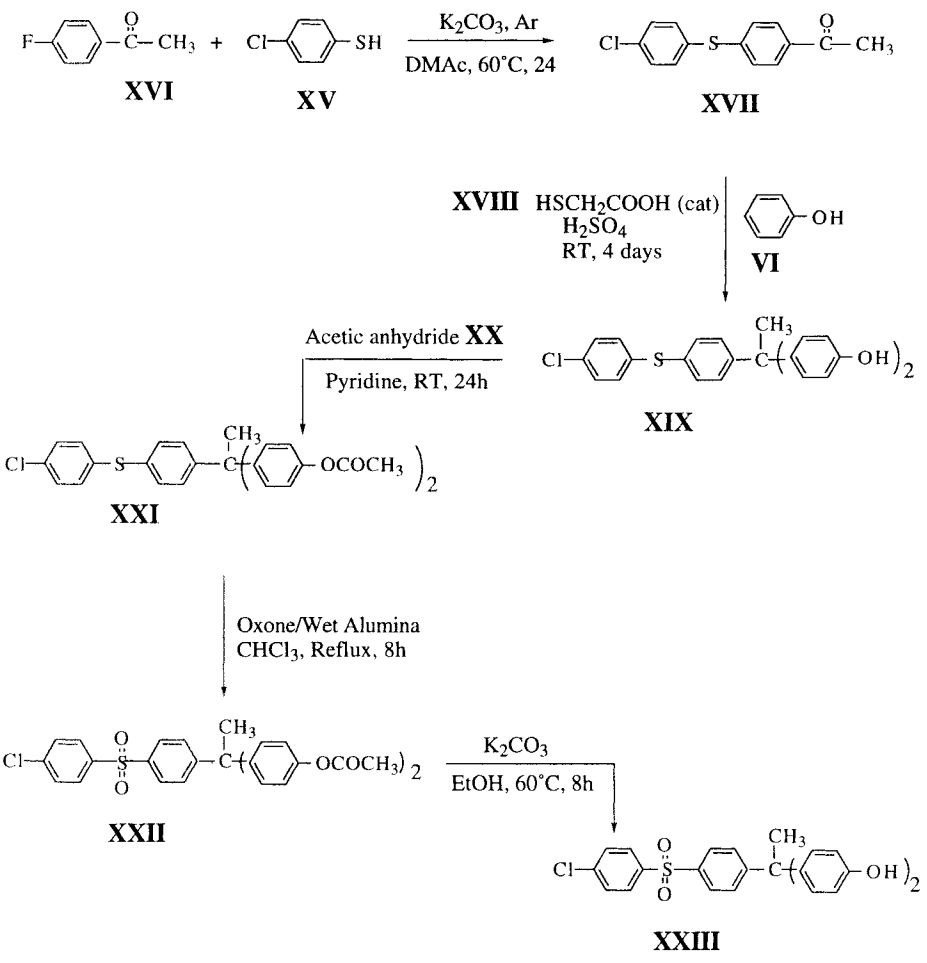
The synthesis of the activated monomer **XIII** is showed in Scheme 4. The reaction begins with the acetylation [29] of the phenol **VII** to protect the phenol during the oxidation of the aryl sulfide groups by Oxone to obtain **XI** and **XII**, respectively. The last reaction is the cleavage of the ester linkages in **XII** using K_2CO_3 to obtain the activated monomer **XIII**. The yield of **XIII** from **VII**, was 56%. NMR and MS characterization of each of these products confirmed the proposed structures.

The reactive oligomer **XIV** is prepared by polycondensation of the activated monomer **XIII** according to the procedure described in Scheme 4. Treatment of monomer **XIII** with an excess of NaH yields a solution of its sodium salt [17]. Heating the NMP solution of the sodium salt under reflux effects polymerization. The isolated yield was 82%.

Scheme 4



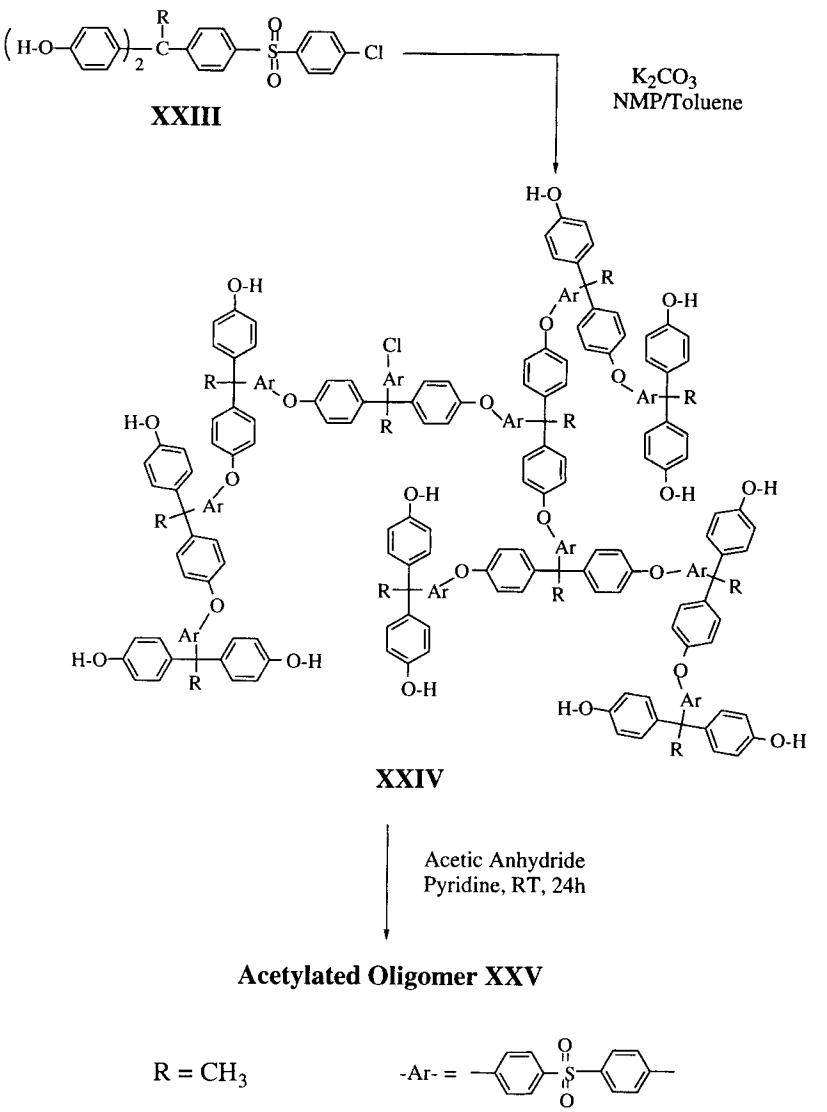
Scheme 5



In a similar way, the synthesis of phenol-terminated reactive oligomer **XXIV** was carried out using the divergent uncontrolled method. The reactive oligomer can be readily obtained by self-condensation of bisphenols **XXIII** (Scheme 3) using the one-pot approach. This relatively high molecular weight A_2B monomer is a bisphenol which contains a single aryl chloride activated by a sulfone moiety.

The synthesis of the monomer **XXIII** is shown in Scheme 5. The reaction began with the displacement of the fluoride of 4-fluoroacetophenone **XVI**, by a molecule of 4-chlorothiophenol **XV**, using K_2CO_3 under mild conditions [30] to obtain the condensation product **XVII**. In the following step the bisphenol **XIX** was

Scheme 6



formed by condensation of **XVII** with two molecules of phenol **VI** employing H_2SO_4 and mercaptoacetic acid **XVIII** as catalyst at room temperature [31]. The last three reactions employed were the acetylation of the phenol, followed by the oxidation of the aryl sulfide groups by Oxone, and finally cleavage of the ester linkages of **XXII** to generate the activated monomer **XXIII** using K_2CO_3. The

TABLE 1. Some Characteristics and Properties of Compounds **IX** and **X**

	IX	X
FW (g/mol)	1458	1586
MW(MALDI)[a]	1463	1590
Mw (g/mol)[b]	706	1042
PD[b]	1.06	1.09
η_{inh} (dL/g)[c]	0.06	0.06
Tg (°C)[d]	102	168
Yield (%)	82	95

[a] Dithranol: Sample: CF_3CO_2Ag = 40:4:1.
[b] SEC, based on polystyrene standards, $CHCl_3$, 1mL/min, UV-detector; data from crude products; data from purified samples.
[c] NMP, 0.5 g/dL, 25 °C.
[d] N_2, 10 °C/min.

overall yields in the synthesis of the monomer **XXIII** from **XVI** was 27%. NMR, and MS characterization of each of those products confirmed the proposed structures (see Experimental Section).

The reactive oligomer **XXIV** was prepared by polycondensation of the activated monomer **XXIII**. The monomer **XXIII** was polymerized using K_2CO_3 in NMP/toluene under N_2 atmosphere according to the general procedure described in Scheme 6. K_2CO_3 was the condensation agent since the preformed bisphenolate was not easy to prepare. The yield of **XXIV** was 78%.

Molecular Characterization of Products (Generation = 0) IX and X

The weight average molecular weights (Mw's), and polydispersities (PD's) of the purified compounds **IX** and **X** are given in Table 1. The polydispersity values, PD's, as measured by SEC, remain close to 1 as is expected for almost monodisperse materials. There is a significant difference between the weight average molecular weights and the formula weights (FW) of the compounds. This can be explained if we assume that their structures are more compact than those of the polystyrene standards used in the calibration curve.

Scheme 7

Terminal Unit A **Terminal Unit B**

For the discussion of the NMR characterization of the these products it is useful to describe the building units that make up these compounds (Scheme 7). The nomenclature proposed by Newkome was taken into account to describe their structures [32]. The numbers in Scheme 7 were arbitrarily chosen and represent the different hydrogens in the compounds. Cosy experiments were carried out for the identification of the protons. The differences between the ^1H NMR (500MHz) spectra of compound **IX** and compound **X** confirm that structural changes occurred during the oxidation reaction. The ^1H NMR data show that before the oxidation reaction protons H_{12} and H_{13} at the terminal units A absorb at [a] 7.34 ppm and 7.4 ppm (Figure 1a). After the oxidation reaction these protons, now close to the new sulfone group (terminal unit B : H_{10} and H_{11}), show resonances at a δ = 7.94 ppm and 7.66 ppm (Figure 1b). The differences between theoretical and experimental values of the integrals are $\leq$ 5%.

The ^{13}C NMR (50MHz) results are similar. For example, before the oxidation reaction atoms C_1, C_4, and C_5 at the terminal unit C absorb at about δ = 134 ppm. After the oxidation reaction these carbons, now close to the new sulfone group (terminal unit D), show resonances at about δ = 140 ppm (see Experimental Section).

MALDI-TOF-MS, a technique which is becoming of increasing importance for synthetic polymer chemistry [33], was used for the mass determination of the aryl ethers. The analyses were carried out on a Kratos Compact MALDI III instrument in the reflectron mode using dithranol as the matrix. Silver trifluoroacetate was added to stabilize the system. Figure 2 show the quality of the spectrum. The molecular ion masses, MI's, of aryl ether sulfide and aryl ether sulfone compounds are given in Table 1.

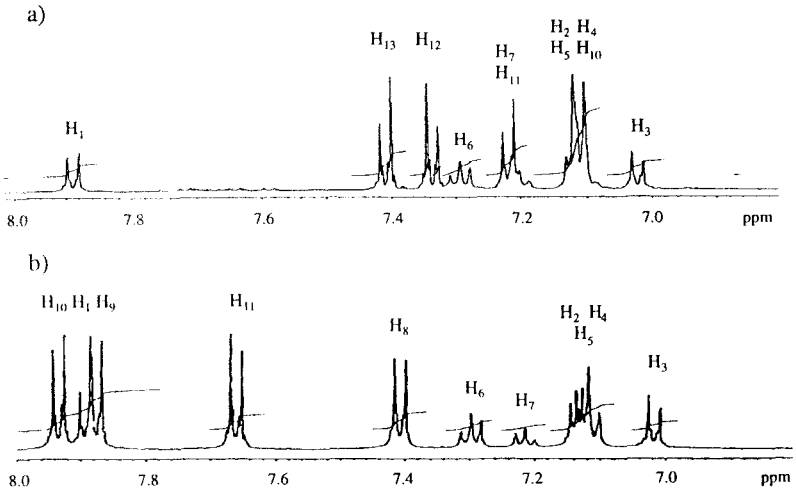


Figure 1. ^{1}H NMR spectra of: a) **IX**, b) **X**.

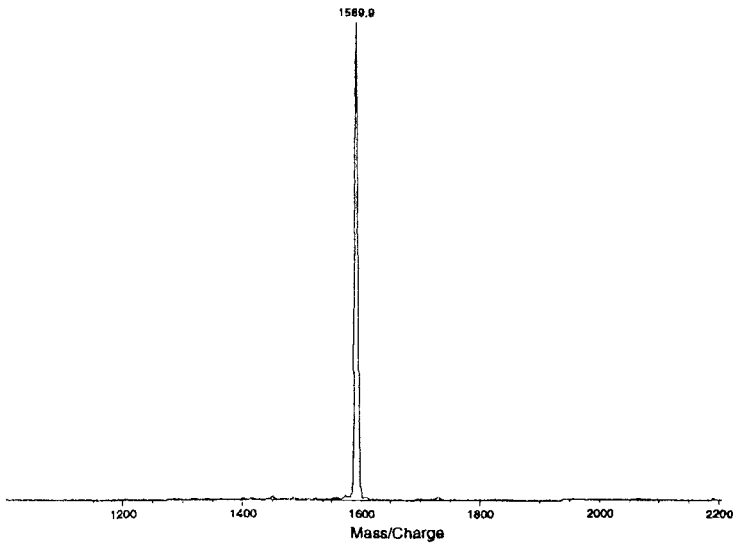


Figure 2. MALDI-TOF-MS of **X**.

The mass spectra of **IX** and **X** show only one main signal (peak 1) which corresponds to the molecular ion. The differences between the calculated and found values can be explained assuming that a lithium cation (7 Da) is complexed with a molecule of the sample. Lithium cations can come from the metallic sample holder used for the analysis. Silver cations are not detected, probably due to the low concentration of CF_3CO_2Ag used. However, it is absolutely necessary to use this reagent to avoid the fragmentation of the sample. Taking this fact into account , the mass differences between the calculated and the experimental values are around 0.1%.

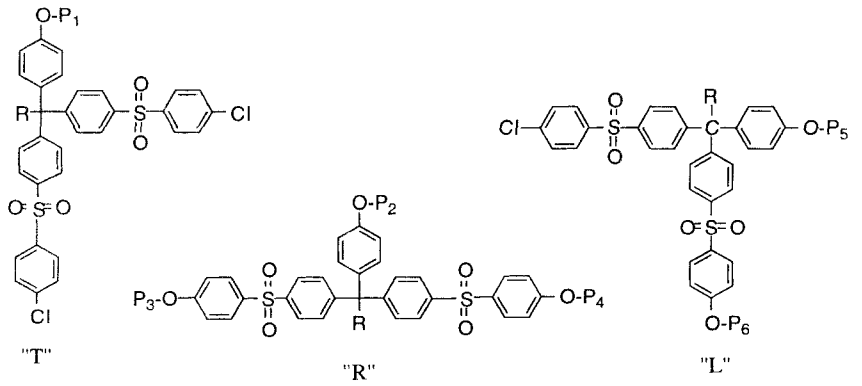
The data accumulated indicate that the conditions employed in the reactions are efficient for the syntheses of **IX** and **X** since no signals were detected for the reaction intermediates; only the molecular ions were observed. Elimination of Cl^- by reductive elimination was not detected.

NMR Characterization of Hyperbranched Oligomers

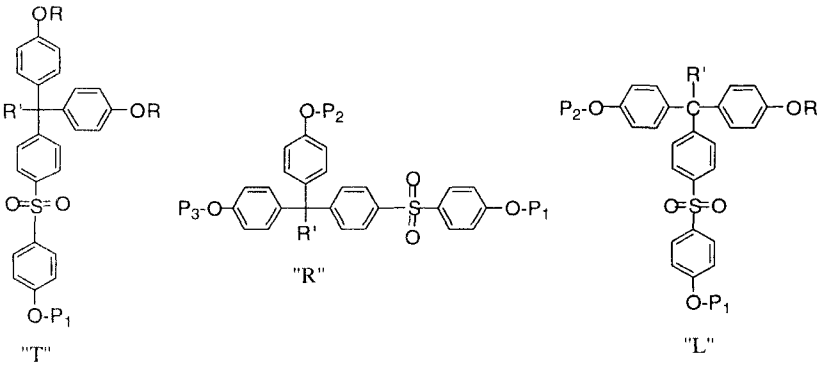
The three building blocks that make up the hyperbranched oligomers synthesized are shown in Scheme 8. Their structures consist of terminal units (T), lineal units (L), and branching points (R). However, due to the complexity of these systems only a general assignment of the absorption to the different protons or carbons in these molecules was possible. The broad molecular size distribution of these samples led to significant peak broadening in their ^1H NMR spectra. To simplify this study, we chose the lineal block "L" to describe the NMR spectra. This is the only block that can generate all the different possible signals in the compounds. The numbers in the structure shown in the ^1H NMR figures represent the different hydrogens on the molecules.

The ^1H NMR spectra and Cosy experiments obtained for monomers **XIII** (See Experimental Section) and that of **XIV** (Figure 3) confirm their general structures. Reactive oligomer **XIV** shows signals that corresponded to those of the more regular dendritic compound **X**. The aromatic protons ortho to the sulfone group (H_7, H_8, H_{10}) resonate at about 7.9 ppm and the aromatic protons ortho to the chloride (H_9) resonate at about 7.6. The high intensity and broadness of the peaks of the aromatic protons close to the oxygen suggests that the displacement of the halides took place and that ether linkages were formed. The same general conclusions are obtained from the ^{13}C NMR results. For example, there are two important signals for C's at the ß positions from oxygen atoms (C_1, C_2) which resonate at about 118 ppm and 119 ppm, but there is only a single signal for carbons of that type in the monomer (see Experimental Section). This carbon (C_2) resonates at about 115 ppm.

Scheme 8



P = oligomer segments, R = phenyl.



P = oligomer segments; R = H, acetyl; R' = methyl.

The ^{1}H NMR spectra of monomers **XXIII** and that of **XXIV** also confirm their general structures. The spectrum of **XXIII** (Figure 4a) shows resonances corresponding to HO-C_6H_4- terminal groups (H_6, H_7). The fact that the resonance of the aromatic protons ortho to the chlorides, H_1, present in the monomer (7.4-7.5 ppm) disappeared in the reactive oligomer (Figure 4b) and the peaks of the aromatic protons close to the ether bonds in the reactive oligomer (H_1, H_2, H_9, H_{10}) are intense suggest that the displacement of the chlorides took place and that ether linkages were formed.

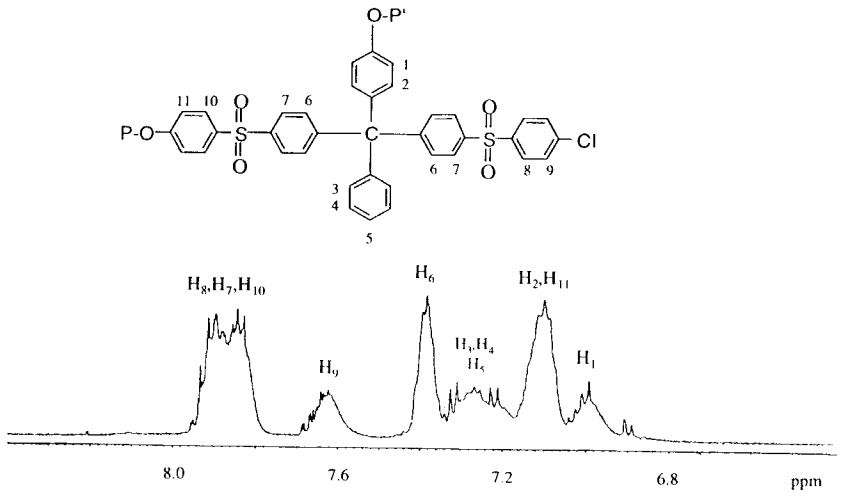


Figure 3. ^{1}H NMR spectrum of **XIV**. P and P' are oligomer fragments.

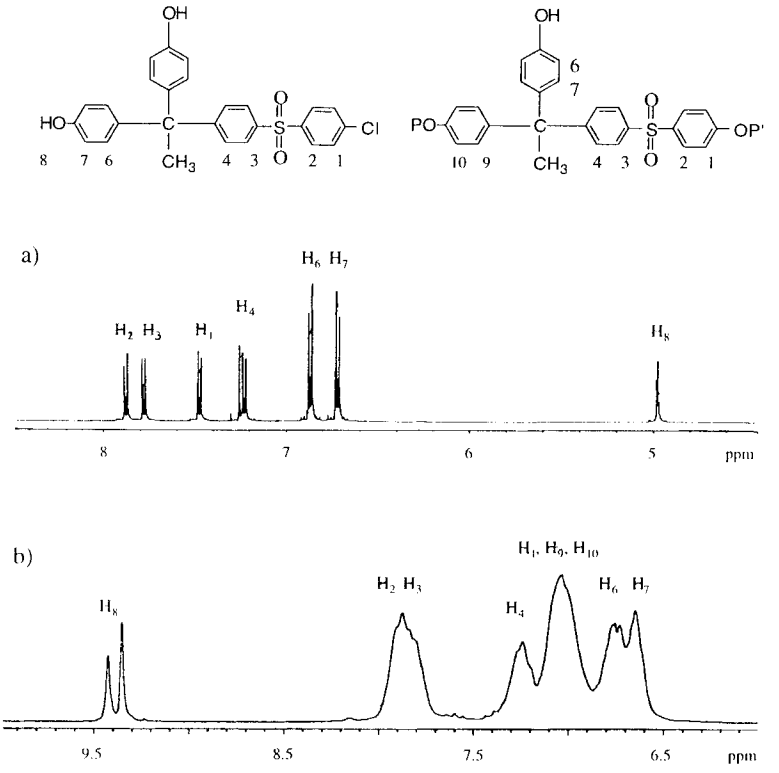


Figure 4. ^{1}H NMR spectra of: a) **XXIII** and b) **XXIV**. P and P' are oligomer fragments.

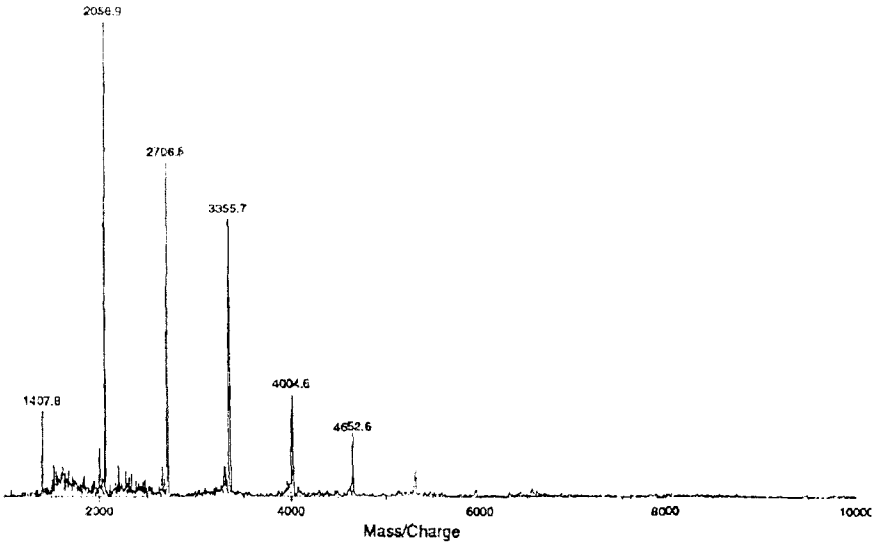


Figure 5. MALDI-TOF-MS of **XIV**.

The reactive oligomer XXIV contains multiple chain ends with phenolic groups which have a high reactivity and can be converted into the corresponding acetyl esters. This modification changes the solubility of the oligomer and it is useful in its SEC characterization. Acetylation of **XXIV** with acetic anhydride and pyridine gave the acetyl-terminated oligomer **XXV**. The absence of the phenolic O-H stretch at 3300 cm^{-1} in the IR spectrum indicates that the functionalization was complete. In contrast to the phenol-terminated oligomer which is soluble in polar solvents such as THF and DMF, the acetylated oligomer is soluble in $CHCl_3$ and toluene.

The ^1H NMR spectrum of **XXV** (see Experimental Section) and Cosy experiments are in agreement with the proposed structures. The signals for the aromatic protons closer to the sulfone groups (H_2, H_3) resonated at about 7.8 ppm. The aromatic protons closer to the oxygen (H_1, H_7, H_{10}) and to the quaternary carbons (H_4, H_6, H_9) range from 7.5 ppm-6.7 ppm, while the resonances for the methyl protons are seen near 2.1 ppm. The same general conclusions are obtained from the ^{13}C NMR spectrum of **XXV**. For example, there are three signals for C's at ß positions from oxygen atoms (C_1, C_2, C_3) in the acetylated product which resonate at about 122 ppm, 120 ppm, and 118 ppm but there is only a single signal for that type of carbon in the monomers (see Experimental Section). This carbon, C_1, resonates at about 115 ppm.

MALDI-TOF-MS Characterization of Hyperbranched Oligomers

MALDI-TOF-MS was used for the mass determination of **XIV** (Figure 5) and **XXIV** and **XXV** (Figure 6). The analyses were carried out in a similar way to that described for the analyses of **IX** and **X**. We see evidence for the formation of oligomers with degree of polymerization between 2 and 12. However, by this method we can not exclude the possibility that higher molecular weight material may have been formed.

The values of mass/charge found correspond to the oligomeric molecular ions (a silver cation is complexed with each of the sample molecules). The molecular masses, M's of **XIV** and **XXIV** (Table 2) were calculated using the following general equation:

$$M(n) = n(A - B) \text{ Da}$$

In this equation, n represents the degree of polymerization of the oligomer, A is the molecular mass of de monomer (**XIII:** 685.7 Da, **XXIII**: 465.0 Da), and B is the molecular mass of the small molecule eliminated during the condensation reaction (HCl: 36.45 Da).

In general, when n molecules react to generate n ether linkages, n-1 molecules of HCl are eliminated. In the present case, there were lost n and not n-1 molecules of HCl. Since the ^{1}H NMR spectra of **XIV** do not show any evidence of a hydroxyl group in the reactive oligomer, the probable termination reaction is the displacement of a chloride by the only hydroxyl group present in the molecule (internal cyclization). However, reductive dechlorination cannot be excluded as a possible side reaction since if an atom of chloro is displaced by an atom of hydrogen the differences between the calculated molecular masses and the experimental values of mass/charge are still reasonable.

The MALDI results for **XXIV** and **XXV** (Figure 6, Table 2) are similar to those found previously for aryl halide-terminated reactive oligomer **XIV**. This system lost n and not n-1 molecules of HCl, as expected according to the stiochiometry of the reaction. An intramolecular reaction between the activated aryl chloride with one of the many phenolates surrounding it in the same molecule would be expected to occur.

The molecular ion masses, M's, of the acetylated reactive oligomer were calculated using the following equation:

$$M(n) = n(A - B + C) \text{ Da}$$

where C = 42 Da. This value, as expected, corresponds to the mass

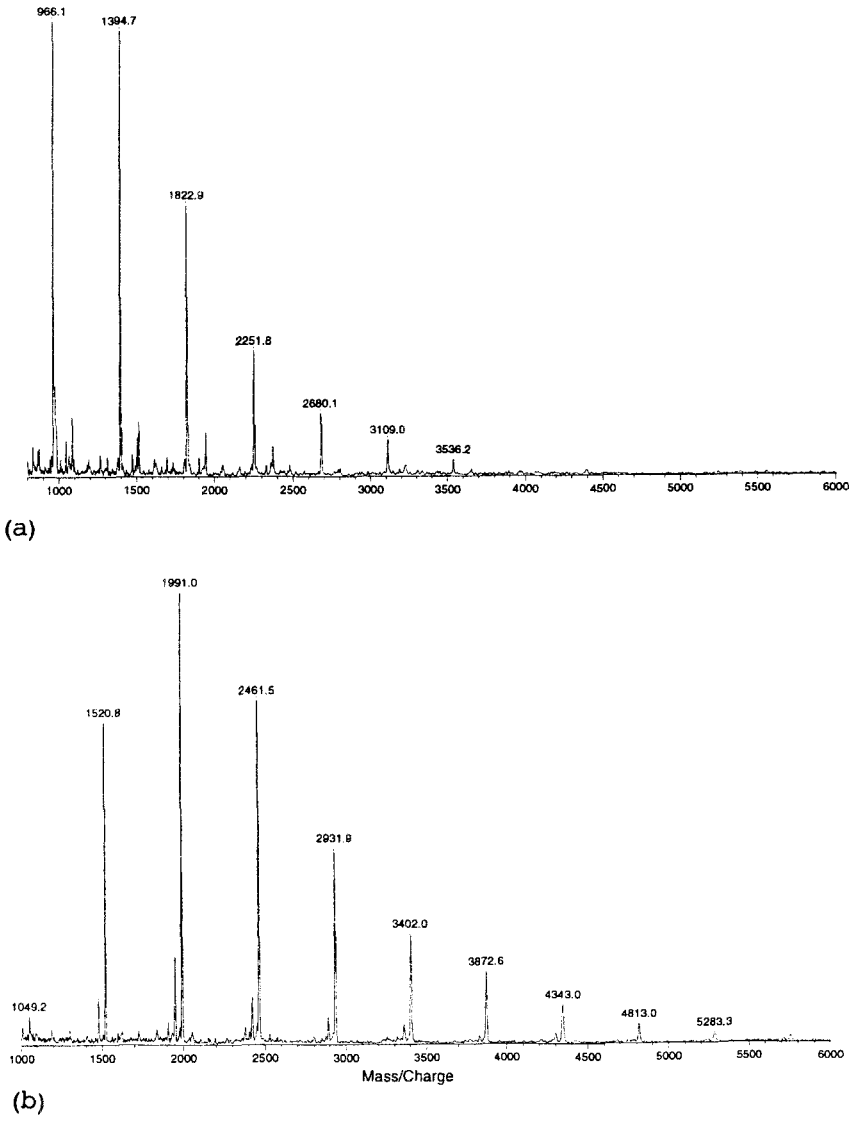


Figure 6. MALDI-TOF-MS of: **XXIV** and b) **XXV**.

difference between the acetate group (59 Da) and the hydroxyl group (17 Da). The small peak that accompanies each of the intense signals present in the MALDI mass spectrum of **XXV** could be a consequence of a fragmentation of the molecule with loss of an acetyl group.

For all these systems, the differences between the calculated values (MI + Ag) and the experimental values (mass/charge) are about 0.1%. The MALDI data

TABLE 2. MALDI-TOF-MS Analyses of **XIV**, **XXIV**, and **XXV**[a]

	XIV		**XXIV**		**XXV**	
n[b]	$(M+Ag)^+$ [c]	Mass/Charge	$(M+Ag)^+$ [c]	Mass/Charge	$(M+Ag)^+$ [c]	Mass/Charge
2	1406.5	1407.8	965	966.1	1049	1049.2
3	2055.75	2056.9	1393.5	1394.7	1519.5	1520.8
4	2705	2706.5	1822	1822.9	1990	1991
5	3354.25	3355.7	2250.5	2251.8	2460.5	2461.5
6	4003.5	4004.6	2679	2680.1	2931	2931.9
7	4652.75	4652.6	3107.5	3109	3401.5	3402
8	5302	5301.5	3536	3536.2	3872	3872.6
9	5951.25	5950	-	-	4342.5	4343
10	-	-	-	-	4813	4813
11	-	-	-	-	5283.5	5283.3
12	-	-	-	-	5754	5750

[a] Dithranol:Sample:CF_3CO_2Ag = 40:4:2.
[b] n = degree of polymerization.
[c] M= molecular mass, Da; Ag = silver atomic mass, Da.

was very useful in the identification of the termination reaction and characterization of the lower molecular weight species formed during the polymerization reaction.

SEC Characterization of Hyperbranched Oligomers

The molecular masses were measured by SEC relative to polystyrene standards. The shape of the SEC chromatograms of **XIV** and **XXV** (Figure 7) showed overlay peaks which indicated that species with very different molecular weight and size were present in these samples. Since the chromatograms are not represented by Gaussian curves, the data obtained gives only a rough idea of the molecular characteristics of these polymers. The weight average molecular weight and the polydispersities of the aryl chloride-terminated reactive oligomer **XIV** and the acetyl-terminated reactive oligomer **XXV** are given in Table 3.

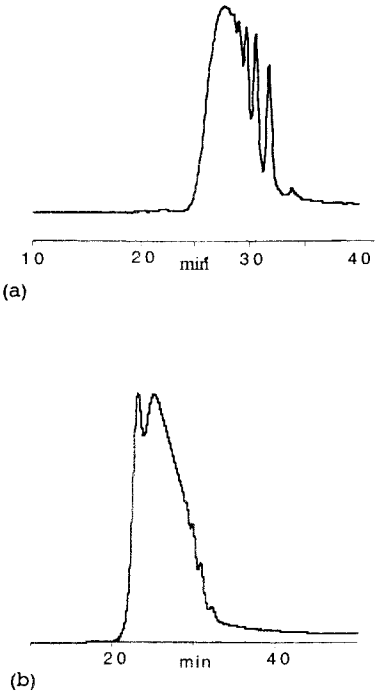


Figure 7. SEC chromatograms of: **XIV** and b) **XXV**. Analysis conditions in Table 3.

TABLE 3. Some Properties and Characteristics of **XIV**, **XXIV**, and **XXV**

	XIV	**XXIV**	**XXV**
C (mol/L) [a]	0.20	0.5	-
η_{inh} (dL/g) [b]	0.10	0.25	0.22
Tg (°C) [c]	226	261	242
Td (°C) [c]	462	395	420
Mw (g/mol) [e]	4800	-	20200
PD [e]	2.2	-	4.6

[a] Monomer concentration
[b] Inherent viscosity, NMP, 0.5 g/dL, 25°C.
[c] N_2, 10 °C/min.
[d] 5% loss weight, 10 °C/min.
[e] SEC, based on polystyrene standards, chloroform, 1mL/min, UV-Detector.

Monomer concentrations of **XIII** and **XXIII** higher than 0.2 mol/L and 0.5 mol/L, respectively, yielded some insoluble materials in the condensation reaction. The lower concentration required for monomer **XIII** could be a consequence of a lower solubility of **XIV** in the medium of the reaction. Below these values an increase in monomer concentration causes a corresponding increase in molecular weight. These results also suggest that unimolecular termination reactions have apparently occurred. At low concentrations, intramolecular cyclizations would be expected to be favored which could generate low molecular weight species. However, insoluble materials can be formed at higher concentrations since bimolecular reactions are favored, yielding high molecular weight polymers and high viscosity reaction mixtures.

Properties

Thermal properties were studied by DSC and TGA, (Tables 1 and 3). For the hyperbranched oligomers, we observed a T_g around 225°C-260°C but no evidence for melting or crystallization in these materials. TGAs under N_2 at 10°C/min showed that they retain 95% of their mass up to 395°C-460°C. These properties are similar to those of linear poly(ether ketone)s and poly(ether sulfone)s. The thermal stability of the phenol-terminated reactive oligomer **XXIV** is lower than that of its acetylated product and that of the aryl halide-terminated reactive oligomer **XIV**. This can be a consequence of the lower stability of the terminal phenol groups. The stronger intermolecular interactions between the terminal -OH groups in **XXIV** probably cause the relatively higher T_{gs} compared to that obtained for aryl halide-terminated or acetylated hyperbranched oligomers. Since compound **X** has a more polar structure, its T_g is higher than that of **IX** (168°C vs 102°C).

As expected, the inherent viscosity of **XIV** is higher that that of **X** due to the higher molecular weight species formed in the one-pot reaction. The phenol-terminated sample shows higher inherent viscosities than that of the aryl chloride-terminated reactive oligomer, probably due to higher molecular weight species present in the sample and a stronger interaction with the solvent.

CONCLUSIONS

We have carried out the synthesis of tetrafunctional aryl ether sulfones **IX** and **X**, from bis(4-fluorophenyl)sulfone and a relatively high molecular weight preformed sodium bis(chloroaryl)phenolate. The polycondensation of A_2B monomers **XIII** and **XXIII** via a one-pot approach has been shown to be a route for the

formation of hyperbranched oligomers possessing high thermal stability with aryl chloride or phenol terminal functionality. The syntheses of the monomers and hyperbranched oligomers are easily carried out and produce the products in relatively high yield.

MALDI-TOF-MS confirmed the proposed general structure for the products and also allowed us to obtain the degree of polymerization of the oligomeric species present in the samples. The results also indicated that an intramolecular cyclization competed with the polymerization reaction of the activated monomers. NMR characterization also confirmed the proposed structure for all these products.

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