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Registry No. $KMg_3[Si_3AlO_{10}]F_2$, 12003-38-2; Mg_2SiO_4, 15118-03-3.

Convergent Synthesis of Monodisperse Aryl Ester Dendrimers

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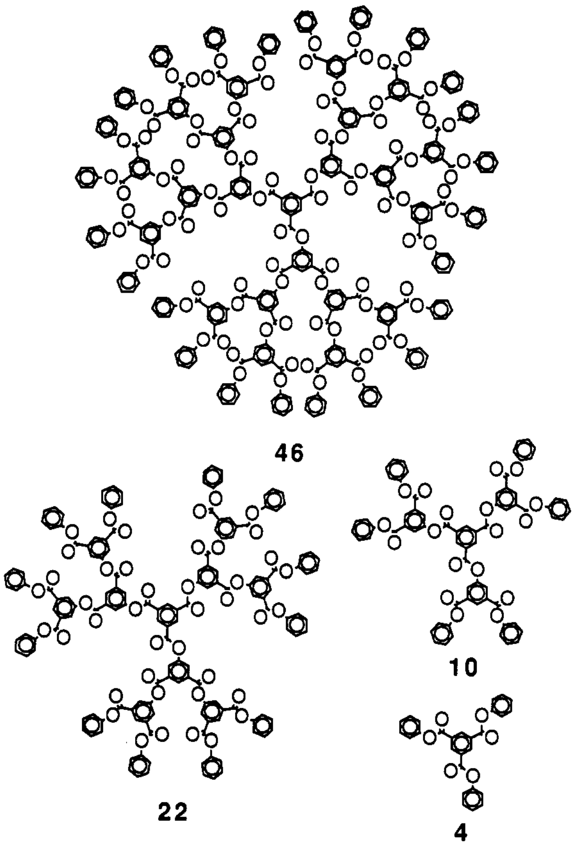
We describe here the convergent synthesis of a new family of starburst dendrimers based upon 1,3,5-linked aryl esters. Starburst polymers differ from conventional linear polymers in that each monomer unit except for the terminal units is a branch point. The original route to starburst dendrimers is divergent and involves attaching geometrically increasing numbers of reactants to the outside of a molecule having geometrically increasing numbers of reactive groups.[1-3] Tomalia has successfully made polymers up to approximately 10 generations using this technique.[1] The difficulty with this approach is that at higher generations, it becomes nearly impossible to get complete reaction at all of the functional groups. We and others have recently developed a convergent synthetic route to starburst dendrimers.[4-6] The convergent synthetic scheme involves the synthesis of progressively larger dendrons that are prepared by attachment of a small number (typically two) of smaller dendrons to a molecule having two kinds of functional groups, X and Y. A dendron has a functional group Z that reacts with one of the two kinds of functional groups, let us say X, in the molecule. The functional group Y in the new larger arm must then be converted to the functional group Z, allowing another iteration to be carried out or allowing the dendrons to be assembled around a core containing a small number (typically three) of the functional group X. The advantages of the convergent approach have been discussed and include the ability to precisely control molecular weights and the possibility of making materials having functionalities in precise positions and numbers within these materials.[4-7] A limiting factor for the synthesis of larger dendrimers by the convergent route may be that the single functional group needed for the next generation may be buried within the dendron and thus be inaccessible for reaction. The first system we reported on consisted of only 1,3,5-linked benzene rings and is the first all-hydrocarbon starburst dendrimer.[4] We believe that beyond a certain generation these molecules should become essentially spherical and have proposed that these materials may be used as size standards in the 20–50-Å size regime. We have obtained preliminary evidence by dynamic light scattering that these compounds behave as if they were small uniform spheroids.[8] The synthetic strategies reported here may be useful in the preparation of complex, ordered molecular structures capable of carrying out energy conversion or information storage.

Scheme I



We have prepared a series of four aryl ester based dendrimers (Scheme I) having 4, 10, 22, and 46 phenyl rings, nominal molecular weights of 438, 1159, 2600, and 5483, and diameters of 19, 30, 37, and 45 Å, respectively, as determined from examination of space-filling molecular models. (Note: compound 4 is not actually a dendrimer as defined by Tomalia[1] since it possesses no branch sites. It is more properly defined as a star-branched structure). The aryl ester dendrimers have several advantages over the all-aryl dendrimers we described previously.[4] First, formation of ester bonds is significantly easier than formation of aryl–aryl bonds. Second, the ester linkage provides two extra degrees of freedom, which should permit the preparation of larger molecules because the ester materials are larger at the same generation than the all-aryl dendrimers, and the flexibility of the linkages should sterically permit the synthesis of higher generations. The syntheses of **10**, **22**, and **46** first required the preparation of the dendrons 3-OH, 7-OH, and 15-OH (Scheme II). Because of the cumbersome systematic nomenclature for these molecules, we name them by a number referring to the number of benzene rings in the molecule followed by an abbreviation for the reactive functional group. The

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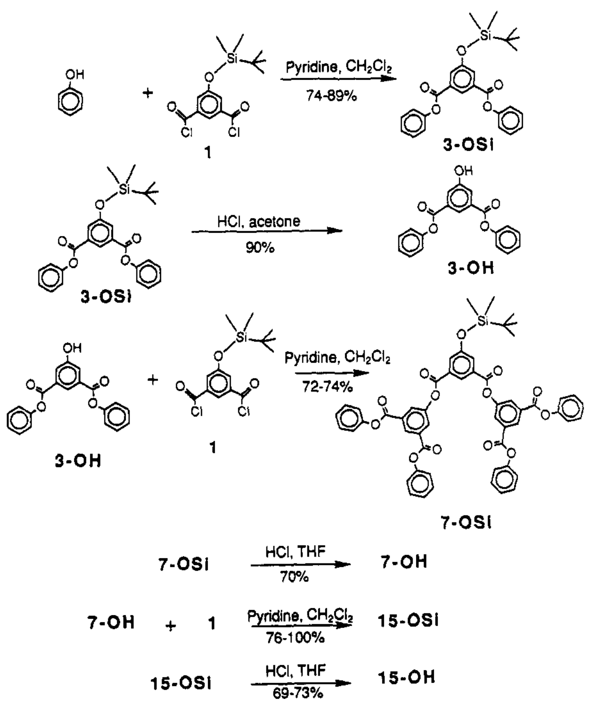
Scheme II



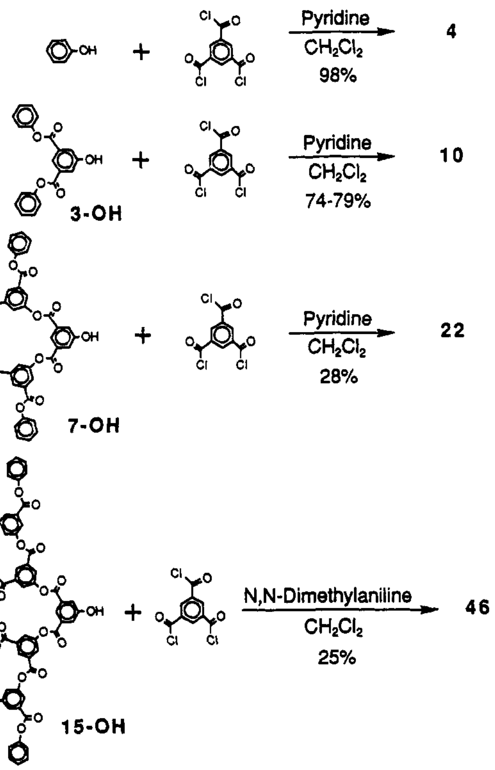
key intermediate in the syntheses of the dendrons is 5-(*tert*-butyldimethylsiloxy)isophthaloyl dichloride, **1**. It was prepared in three steps, in overall yield of 75–93% beginning with commercially available 5-hydroxyisophthalic acid. The hydroxyl and carboxyl groups of this compound were protected with the *tert*-butyldimethylsilyl group using *tert*-butyldimethylsilyl chloride and imidazole in DMF. The ester groups were then selectively cleaved by using acetic acid/water/tetrahydrofuran, and the resulting diacid was converted to the chloride with $SOCl_2$.

Preparation of the dendrons used the iterative sequence of esterification and hydrolysis reactions shown in Scheme II. Reaction of **1** with phenol yielded diphenyl 5-(*tert*-butyldimethylsiloxy)isophthalate, **3-OSi**. Typically *tert*-butyldimethylsilyl ethers are cleaved with fluoride ion in THF, and this procedure worked well in the synthesis of **3-OH** but failed in the deprotection of larger dendrons. Reaction of **7-OSi** with fluoride ion yielded a complex mixture of phenols containing substantial amounts of **3-OH** and the unsymmetrical phenol containing five phenyl rings in addition to **7-OH**. Reaction of an acetone or THF solution of the protected dendrimer arms, **7-OSi** or **15-OSi**, with 1 N HCl yielded the deprotected phenols, **7-OH** or **15-OH**, respectively, cleanly and in high yield.

Compound **4** and the dendrimers **10**, **22**, and **46** were prepared by reaction of the appropriate dendron with 1,3,5-benzenetricarbonyl trichloride (Scheme III). The choice of base is critical. Pyridine works well in the syntheses of **4**, **10**, and **22**. We were unable to prepare **46** that was free of contaminants using either pyridine or *p*-(dimethylamino)pyridine (DMAP). We found that ester interchange occurs in the synthesis of **22** when DMAP is used instead of pyridine because we were able to isolate compounds containing 18 and 26 phenyl rings as well as **22** by careful column chromatography. These compounds are most simply obtained by interchange of **3-OH** and **7-OH**. We infer that ester interchange is also the problem in the synthesis of **46**. Use of the weaker and less nucleophilic base *N*,*N*-dimethylaniline eliminated ester interchange and afforded **46** cleanly.

Compound **4** is known, but **10**, **22**, and **46** are new materials and are fully characterized.[9] Because of the high symmetry of these molecules, ^1H NMR spectroscopy is very useful in confirming the structure and assessing the purity of these materials. Spectra for **4**, **10**, **22**, and **46** are shown in Figure 1, and each of the protons even in **46** is well resolved from its neighbor. As in the all-aryl den-

Scheme III



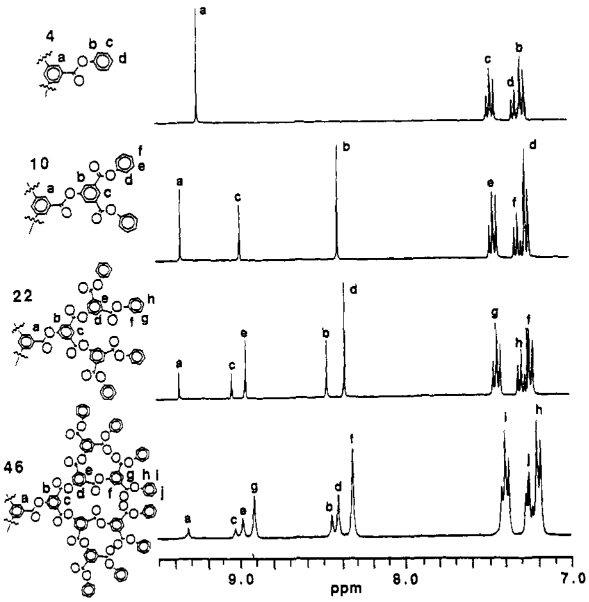


Figure 1. ^1H NMR spectra of dendrimers in $CDCl_3$ at 360 MHz.

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[9] Compound **4**: mp 176–178 °C; ^{13}C NMR ($CDCl_3$) δ 163.38, 150.55, 136.07, 131.22, 129.67, 126.36, 121.51. Compound **10**: mp 140–146 °C; ^{13}C NMR ($CDCl_3$) δ 163.23, 162.69, 150.73, 150.55, 136.66, 132.09, 130.78, 129.63, 128.21, 126.32, 121.48. Anal. Calcd for $C_{69}H_{42}O_{18}$: C, 71.50: H, 3.65, O, 24.85. Found: C, 71.26; H, 3.83; O, 25.11. Compound **22**: mp 153–168 °C; ^{13}C NMR ($CDCl_3$) δ 163.21, 162.70, 162.51, 150.91, 150.72, 150.51, 132.01, 131.33, 130.66, 129.62, 128.85, 128.19, 126.30, 121.47. Anal. Calcd for $C_{153}H_{90}O_{42}$: C, 70.67; H, 3.49; O, 25.84. Found: C, 70.32; H, 3.73; O, 26.09. Compound **46**: mp 193–202 °C; ^{13}C NMR ($CDCl_3$) δ 163.12, 162.61, 162.47, 150.86, 150.67, 150.49, 131.91, 131.19, 130.58, 129.54, 129.35, 128.73, 128.12, 126.22, 121.44. Anal. Calcd for $C_{321}H_{186}O_{90}$: C, 70.32; H, 3.42; O, 26.26. Found: C, 70.02; H, 3.31; O, 26.12.

drimers, protons closer to the center of the molecule resonate downfield of those further away.[4] We have further characterized 2-4 by ^{13}C NMR spectroscopy, elemental analysis, and gel permeation chromatography. Gel permeation chromatograms of the dendrimers demonstrate their high purity and the smooth progression of retention times with molecular weight.

These materials are all white microcrystalline or glassy solids that are highly soluble in organic solvents such as dichloromethane, chloroform, THF, ethyl acetate, and toluene. Despite the fact that the molecular weight of **46** is nearly 10 times larger than that of **4**, their melting points differ very little. Compound **46** melts from 192-203 °C and does not readily flow in its molten state, whereas **4** melts sharply at 176-178 °C. We are pursuing the synthesis of higher generations of these dendrimers in order to establish the limits of this approach and are characterizing the thermal and light-scattering properties of the present materials.

Registry No. **1**, 135340-02-2; **3**-OSi, 135340-03-3; **3**-OH, 135340-04-4; **4**, 7383-70-2; **7**-OSi, 135340-05-5; **7**-OH, 135340-08-8; **10**, 135340-09-9; **15**-OSi, 135340-06-6; **15**-OH, 135340-07-7; **22**, 135340-10-2; **46** (homopolymer), 135426-00-5; phenol, 108-95-2; 1,3,5-benzenetricarbonyl trichloride, 4422-95-1.

Synthesis and Polymerization of Propargylamine and Aminoacetonitrile Intercalation Compounds

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Layered inorganic solids (e.g., $M(O_3POH)_2$, MX_2, MOCl, MO_3; M = transition metal, X = chalcogenide) can intercalate organic guest molecules and ions to form layered solids with alternating inorganic and organic layers.[1] Alkylamines intercalate as bilayers between adjacent inorganic host layers. Interaction of the intercalated guest with the host can alter the optical, electronic, or magnetic properties of both the host and guest.[2] Pyrrole, 2,2′-bithiophene,[3] aniline,[4] acrylonitrile,[5] and diene[6] guests have been polymerized in intercalation compounds under suitable conditions. Day[7] and Tieke[8] demonstrated that diacetylenic guest molecules between MX_4^{2-} layers (M = Cd, Mn; X = halide) can be polymerized when irradiated with UV light or γ-rays, giving a material with alternating inorganic and polydiacetylene layers. While the orientation of the diacetylenic molecules in these materials allowed solid-state polymerization to occur, similar materials with monoacetylenic guest molecules did not polymerize. We report herein the intercalation and subsequent polymerization of propargylamine and aminoacetonitrile into $M(O_3POH)_2{\cdot}H_2O$ (M = Zr, Sn).

The acetylenic intercalation compounds were prepared by adding neat propargylamine to a slurry of the host, α-$M(O_3POH)_2{\cdot}H_2O$ (M = Zr, Sn), suspended in water and stirring for 2 days at room temperature. Both the Zr and Sn compounds are colorless and show only a single phase in their powder X-ray diffraction patterns (interlayer spacings of 16.2 and 16.5 Å, respectively). The observed stoichiometries from thermogravimetric analysis in an oxygen atmosphere[9] are $Zr(O_3PO^-)_2(HC{\equiv}CCH_2NH_3^+)_2{\cdot}H_2O$, Zr-CC, and $Sn(O_3PO^-)_2(HC{\equiv}CCH_2NH_3^+)_2{\cdot}H_2O$, Sn-CC. The water found in these materials is presumably in the hexagonal holes of the host phosphate, similar to α-$Zr(O_3POH)_2{\cdot}H_2O$.[10] The aminoacetonitrile intercalates were prepared by adding a 20-fold excess of aminoacetonitrile hydrochloride to a slurry of $M(O_3PO^-Na^+)_2{\cdot}3H_2O$ in water and stirring for 6 days at room temperature to yield grey blue solids. The zirconium aminoacetonitrile compound, Zr-CN, obtained is biphasic with interlayer spacings of 12.9 and 12.0 Å and a stoichiometry of less than two amines per formula unit, $Zr(O_3PO^-)_{1.7}(N{\equiv}CCH_2NH_3^+)_{1.7}(O_3POH)_{0.3}{\cdot}H_2O$. The tin aminoacetonitrile compound, Sn-CN, was single phased (14.7 Å) with a stoichiometry of $Sn(O_3PO^-)_2(N{\equiv}CCH_2NH_3^+)_2{\cdot}H_2O$. These propargylamine and aminoacetonitrile intercalation compounds were characterized by powder X-ray diffraction, elemental analysis, and TGA, as well as FTIR and ^{13}C CPMAS NMR spectroscopies. All of the spectroscopic and analytical data are given in the supplemental material (see paragraph at end of paper).

The intercalation compound Sn-CC prepared in this study is normally an opaque powder. We have found however that a clear crystalline film of Sn-CC can also be prepared. If $Sn(O_3POH)_2{\cdot}H_2O$ (0.75 g) is added to 5.5 mL of a 60% (w/w) aqueous solution of propargylamine and heated at 50 °C for 2 weeks the solid tin phosphate dissolves to give a transparent solution. Mixing an equal volume of water with this mixture, centrifuging, and decanting off the liquid from the top, leaves a clear viscous red liquid which when evaporated on a glass slide gives a clear yellow film. This film is stable in chloroform but irreversibly disintegrates in water to give an opaque suspension. The interlayer separation of this film is 15.3 Å, and its IR and ^{13}C CPMAS NMR spectra are very similar to that of powdered Sn-CC. In a related system, Alberti has demonstrated that α-$Zr(O_3POH){\cdot}H_2O$ can be exfoliated in a 0.1 M propylamine solution.[11] What has presumably happened in the case of Sn-CC is that the $Sn(O_3POH)_2{\cdot}H_2O$ exfoliated in the original solution and, on evaporation of the water and excess propargylamine the tin phosphate plates settled to give the observed thin film. This thin film does not give the expected ratio of 2 amines per host formula unit but gives 2.3 amines per formula unit,

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