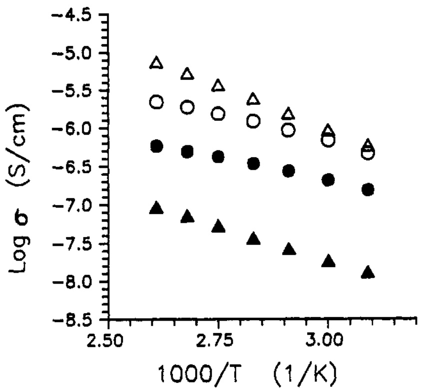
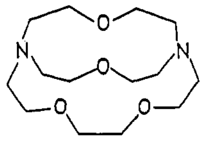
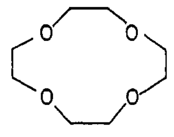


Figure 2. Comparison of the cryptand influence on polymers 1 and 2: (▲) $[NP(OMEE)_{1.77}(OC_2H_4SO_3Mg_{0.5})_{0.23}]_n$, 1; (●) $[NP(OMePEG)_{1.94}(OC_2H_4SO_3Mg_{0.5})_{0.06}]_n$, 2; (○) $[NP(OMePEG)_{1.94}(OC_2H_4SO_3Mg_{0.5})_{0.06}(2.1.1)_{0.06}]_n$; (△) $[NP(OMEE)_{1.77}(OC_2H_4SO_3Mg_{0.5})_{0.23}(2.1.1)_{0.23}]_n$.

mixing weighed amounts of cryptand [2.1.1] (C-2.1.1), A, or 12-crown-4 (12C4), B, and the magnesium poly(phosphazenesulfonate) in acetonitrile. The solution was stirred under a nitrogen atmosphere for 12 h, solvent was then removed under vacuum, and the polymer was first dried under a 0.05-Torr vacuum at 80-90 °C for 2 days and then under 10^{-5} Torr for another 2 days. The techniques employed for ac conductivity and differential scanning calorimetry have been reported previously.[12]



A



B

The conductivity and glass transition temperature (T_g) data for the magnesium ion conductors are listed in Table I. The conductivity of polymer 1, which has the higher ion concentration, is on the order of 10^{-8} S/cm, whereas that of polymer 2 is 10^{-7} S/cm. The glass transition temperatures of polymers 1 and 2, however, are similar. This indicates that in the ion concentration range studied here, the measured T_g's may reflect the microdynamics of the phosphazene backbone and uncoordinated side chains and not the local dynamics in the vicinity of the mobile ion.

The addition of 1 mol of C-2.1.1/mol of magnesium ion to polymer 1 greatly increases the conductivity (Figure 1). As more C-2.1.1 is added, the conductivity further increases and appears to reach a plateau beyond a molar ratio of C-2.1.1 to magnesium of 2 to 1. The addition of C-2.1.1 also increases the conductivity of polymer 2 (Table I). However, the magnitude of enhancement is modest compared with polymer 1. Although the conductivity of 2 is higher than that of 1, addition of the cryptand reverses this order (Figure 2). The glass transition temperatures of polymers 1 and 2 are unchanged by the addition of C-2.1.1. The conductivity of polymer 1 also increases upon addition of 12C4 (Table I), but the increase in conductivity upon the addition of 12C4 is about 6-fold whereas the increase by C-2.1.1 is about 60-fold. It is probable that 12C4 is less effective in reducing ion pairing because of its more open structure, which enables close contact between cations and anions. A Raman study by Doan and coworkers on amorphous PEO and $NaCH_3SO_3$ complexes showed that the SO_3 symmetric vibrational mode shifts from 1085 to 1042 cm^{-1} upon addition of cryptand [2.2.2], whereas addition of 15-crown-5 shifts the vibrational mode by only 4 cm^{-1}.[10] The indicated difference in ion pairing between cryptands and crown ether complexes is also observed in nonaqueous electrolytes.[14]

In conclusion, solvent-free polymeric electrolytes with a magnesium transference number of unity have been synthesized. These magnesium ion polyelectrolytes have low conductivities, but the addition of cryptand [2.1.1] greatly improves the conductivity. A crown ether, 12-crown-4, also increases the conductivity significantly, but the magnitude is much less than that of cryptand [2.1.1]. Apparently, the increase in conductivity upon addition of the complexing agents more than compensates for the presumed decrease in mobility due to the larger effective radius of the metal complex cation. Since the anions are immobile in these systems and the polymer dynamics are essentially not affected by the addition of the complexing agents, the likely origin of the large increase in conductivity is the reduced ion pairing and/or ion aggregation.

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(14) (a) Lehn, J. M. *Pure Appl. Chem.* **1980**, *52*, 2303. (b) Gans, P.; Gill, J. B.; Towning, J. N. *J. Chem. Soc., Dalton Trans.* **1977**, 2202.

Multistep, Sol-Gel Synthesis of a Layered Silicate, Potassium Fluorophlogopite

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Ceramic fiber composites may be an alternative to monolithic ceramics that may fail catastrophically. In such composites, a sufficiently weak fiber matrix interface is needed for good strength and toughness.[1] Graphite and boron nitride, both layered materials, have been used to provide such an interface. Because cracks develop when a composite is stressed, thus exposing the interface to the environment, neither coating is appropriate for extended use at elevated temperatures (>1000 °C) in an oxidizing atmosphere.[2] This problem of oxidative degradation led us to investigate the synthesis of oxidatively stable, layered (sheet) silicates for possible use as fiber matrix interfaces. As oxides, the silicates are inherently stable toward oxidation, and the relatively weak bonds between the layers may provide a sufficiently weak interface. One candidate is the fluoromica potassium fluorophlogopite ($KMg_3[Si_3AlO_{10}]F_2$, KFP). In contrast to natural phlogopite, which decomposes when heated at ca. 800 °C, KFP can be used at temperatures as high as 1200 °C.[3]

Previously, KFP has been synthesized by several methods, all of which involve solid-state reactions.[4] Although these techniques can be used to grow single crystals, they are not appropriate for the formation of very thin coats (<0.5 μm) on fibers. On the other hand, sol-gel

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(1) (a) Kerans, R. J.; Hay, R. S.; Pagano, N. J.; Parthasarathy, T. A. *Ceram. Bull.* **1989**, *68* (2), 429-442. (b) Marshall, D. B. *J. Am. Ceram. Soc.* **1984**, *67* (12), C 259. (c) Marshall, D. B.; Evans, A. G. *J. Am. Ceram. Soc.* **1985**, *68* (5), 225.

(2) Cranmer, D. C. *Ceram. Bull.* **1989**, *68* (2), 415-419.

(3) Zlobik, A. B. In *Kirk-Othmer Encycl. Chem. Technol.*, 3rd ed.; 1981; pp 414-439.

(4) Shell, H. R.; Ivey, K. H. *US Bur. Mines Bull.* **1969**, *647*, 179-183.

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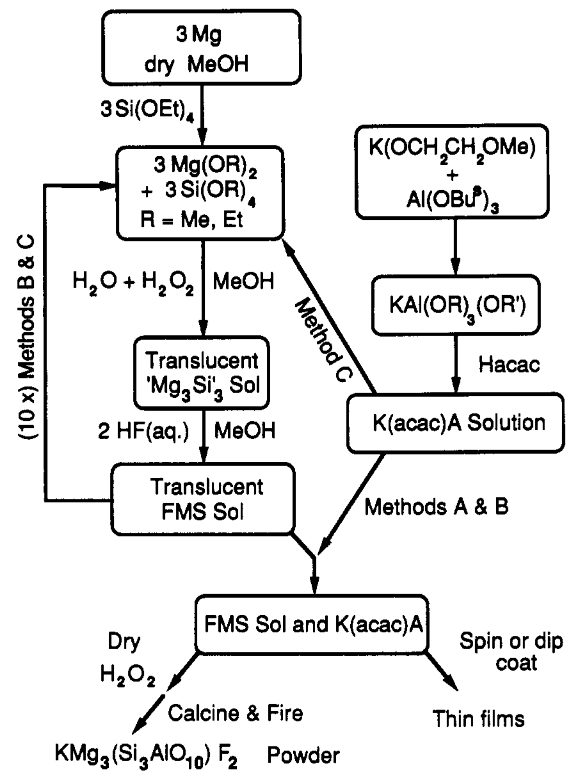
Scheme I



methods have been successfully applied to the preparation of films and coatings on a variety of substrates.[5] We report here the stepwise, sol–gel synthesis of KFP as a first step toward the formation of new, oxidatively stable interfacees for fiber matrix composites.[6]

A precursor for KFP has been prepared by combination of a fluoridated magnesium silicate sol, FMS, and a potassium alkoxyaluminate complex that was modified by acetylacetone, K(acac)A. Three variations of the overall process are illustrated in Scheme I.

The hydrolysis and condensation of a mixture of tetraethylorthosilicate (TEOS) and magnesium methoxide, facilitated by hydrogen peroxide in methanol, has been described for the preparation of sol–gel precursors for synthetic forsterite, Mg_2SiO_4,[7] and enstatite, $MgSiO_3$.[8,9] The principal role of H_2O_2 in these syntheses was to prevent precipitation of $Mg(OH)_2$. A magnesium-containing catalyst, generated in situ, also enhanced the hydrolysis and condensation of TMOS (also generated in situ) during hydrolysis with methanolic H_2O_2.[10]

A partially hydrolyzed, magnesium silicate sol[11] was treated with aqueous HF to facilitate the formation of Mg–F bonds since, in the KFP structure, each fluoride ion is bonded to magnesium.[12] The strategy was to minimize the formation of compounds that contained highly stable Al–F bonds; the bond energy of Al–F is 158 kcal/mol[13] but is only 110 kcal/mol for the Mg–F bond.[14] To further safeguard against reaction of HF with Al, acetylacetone (acacH) was used to form a complex with aluminum. This modification also prevented precipitation of aluminum methoxides when the K(acac)A complex[15] was combined with the FMS sol in methanol. This protocol, referred to as method A, is outlined in Scheme I. When concentrated and dried, the mixture of sol and metal complex formed a clear glass.

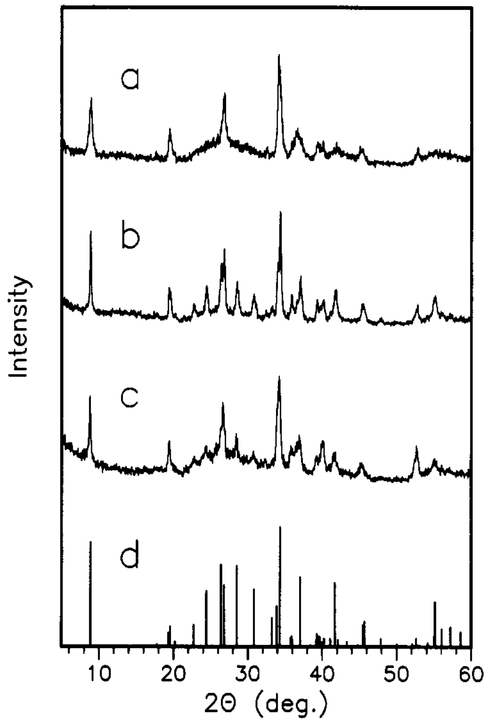


Figure 1. XRD patterns for KFP precursor powders fired at 950 °C: (a) method A; (b) method B; (c) method C; (d) calculated.

For preparation of a powder, the crushed glass was moistened with 30% H_2O_2 to assist in removal of carbonaceous byproducts. Then it was dried, calcined at 600 °C, and fired for 4 h at each of three temperatures, 800, 950, and 1100 °C. X-ray diffraction (XRD) analysis (Figure 1a) indicated the formation of KFP as the principal phase. The slightly broadened peaks suggest that the crystal size is quite small. An amorphous phase is evident from the broad feature in the background at 22–34° (2θ). The presence of forsterite, indicated by peaks at 32 and ca. 40° (2θ), might be caused by either (1) incomplete reaction of HF with the Mg-containing components or (2) decomposition of KFP during the firing process. KFP is known to decompose principally by loss of fluorine through reaction with water in the air, forming forsterite, leucite, and glass.[4] Chemical analysis indicated some loss of fluoride ion at 950 °C (8.45 ± 0.1% F; the theoretical amount is 9.04%).

To preclude the possibility of mistaking phlogopite for KFP due to their very similar XRD patterns, a control

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[5] Brinker, C. J.; Scherer, G. W. *Sol-Gel Science*; Academic Press: Boston, MA, 1990; pp 841ff.

[6] Duldulao, F. D.; Burlitch, J. M., 93rd Annual Meeting of the Amer. Ceram. Soc.; Cincinnati, OH, 1991; Abstr. No. 7JIX-91.

[7] (a) Burlitch, J. M.; Beeman, M. L.; Riley, B.; Kohlstedt, D. L. *Chem. Mater.*, in press. (b) Beeman, M. L.; Burlitch, J. M.; Kohlstedt, D. L. 90th Annual Meeting of the Amer. Ceram. Soc.; Cincinnati, OH, 1988; Abstr. No. 159-B-88.

[8] Burlitch, J. M.; Kohlstedt, D. L.; Riley, B. 91st Annual Meeting of the Amer. Ceram. Soc.; Indianapolis, IN, 1989; Abstr. No. 26-B-89.

[9] Burlitch, J. M. U.S. Patent No. 5,019,293, 1991.

[10] Yeager, K. E.; Burlitch, J. M. *Chem. Mater.* **1991**, *3*, 387.

[11] The partially hydrolyzed magnesium silicate stock sol was prepared in a dry, argon atmosphere by adding 13.3603 g of TEOS (0.0642 mol) to 225 mL of a filtered solution of $Mg(OMe)_2$, formed by dissolving 1.564 g of Mg chips (0.064 mol) in 225 mL of methanol. By means of a syringe pump, 3.435 g of 30% H_2O_2 (0.193 mol of reactive protons counting two from H_2O_2 and one from H_2O), in 35 mL of MeOH was added to the vigorously stirred magnesium silicate solution (1:1 Mg:Si solution) at 1.5 mL/min. The clear, colorless sol obtained was diluted to 500 mL with MeOH.

[12] Takeda H.; Morosin, H. *Acta Crystallogr.* **1975**, *B31*, 2444.

[13] Sanderson, R. T. *Chemical Bonds and Bond Energy*; Academic Press, Inc.: New York, 1971; p 183.

[14] Hildenbrand, D. L. *J. Chem. Phys.* **1968**, *48*, 3657.

[15] A typical K(acac)A solution was prepared by stirring together 5.372 g of aluminum *sec*-butoxide, $Al(OBu^s)_3$ (0.022 mol), in 20 mL of 2-methoxyethanol, and 0.843 g of potassium metal (0.022 mol). The solution was diluted to 100 mL with 2-methoxyethanol.

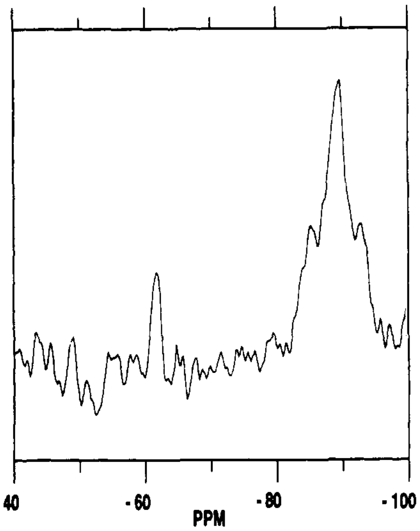

Figure 2. ^{29}Si MAS NMR spectrum of KFP synthesized by method B and fired at 950 °C.

experiment was performed to determine if phlogopite could be synthesized under the same conditions. When water was substituted for HF in method A,[16] analysis of the product by XRD showed the presence of forsterite but no peaks with a high *d* value that could be attributed to a layered silicate.

A multistep addition of HF was devised for the synthesis of the FMS sol to increase the effectiveness of the fluoridation step and to test the validity of (1) above. Method B involved the addition in 10 portions of the following solutions in the order given: (1) 3:3 Mg:Si solution of alkoxides, (2) 30% aqueous H_2O_2 solution in methanol, and (3) 49% aqueous HF solution in methanol.[17] Very little forsterite was observed by XRD analysis even after heating to 950 °C (Figure 1b) or for that matter to 1100 °C. These observations suggest the importance of the efficient mixing of specific reactants to facilitate bonding of fluoride ion to magnesium. Comparison of parts a and b of Figure 1 shows the improvement in crystallinity and phase purity that accrued from this modification. There is less glassy material in the latter as judged by the reduced size of the broad diffraction feature around $2\theta = 30°$.[18] Comparison of the XRD *intensities* in Figure 1b with those found in the literature showed several discrepancies.[19] A good match in both peak positions and intensities with the calculated diffraction pattern (Figure 1d)[20] suggests that the literature values may arise from preferred orientation of the literature sample, a commonly experienced problem during XRD analysis of micas.

Figure 2 shows the magic angle spinning (MAS) ^{29}Si NMR spectrum of KFP that was synthesized by method B. The three peaks at −85.4, −89.7 and −92.9 ppm correspond closely to those of an authentic sample of melt synthesized KFP that had peaks at −85.3, −89.1, −93.3 ppm. The three peaks are due to three Si environments having two, one, and no O–Al bonds in the Si coordination sphere, respectively.[21-23] In addition, an extra peak at −61.9 ppm, assigned to forsterite, is also present.[24]

Aging the sol from method B before gelation had a deleterious effect on the product. Fired gels obtained from a 42-day-old sol gave a noticeably more amorphous product (by XRD). Ligand-exchange reactions could move the fluoride ion to the aluminum where it would presumably stay (see above). Formation of a more crystalline product would probably require higher temperatures or longer heating times or both.

Sols prepared by method B were used to make thin films. The sol was first concentrated by rotary evaporation and then was spin-coated or dip-coated onto a variety of substrates. Multiple coatings were needed to achieve thicknesses of 0.1–0.5 μm. Heating the film at 100 °C for at least an hour between applications, and spinning at a lower rate increased the thickness (measured by ellipsometry).[25] Dip-coating produced films that appeared thicker but were less smooth.

A major problem in the preparation of open (i.e., exposed) KFP films was the loss of fluorine during firing. When a film sample that had been prepared from five coats on a sapphire substrate was fired by using the same heating schedule for powders, the fluorine content was only 2% (as measured by sputtering ESCA analysis). When films were fired for 2–30 min in a preheated tube furnace, the fluoride content was ca. 5%. Thin-film X-ray diffraction analysis at glancing angles showed no evidence for crystalline KFP. TEM analysis of a thin film on a sapphire substrate revealed small amounts of epitaxially oriented forsterite and much amorphous material.[26] Current efforts are directed toward the processing of matrix-encapsulated thin films of KFP.

To test the efficacy of the stepwise addition procedure (i.e., combining magnesium- and fluorine-containing components before addition of any aluminum), another variation was tried. Method C involved adding the K(acac)A solution directly to the solution of magnesium and silicon alkoxides before hydrolysis.[27] The hazy mixture obtained was then added in portions alternately with the H_2O_2 and the HF solutions in methanol, as in method B. While the final sol looked and behaved similarly to that obtained from method B, the XRD pattern (Figure 1c) was noticeably worse. Method C produced some KFP but also gave a greater amount of amorphous material as shown by the broad features in the background between 22 and 34° (2θ). Amorphous products may arise from polymeric precursors that contain Al–F bonds and Al–F–Al bridges.

We are extending the new synthesis methodology to the preparation of other layered silicates. Since the physical properties of micas depend on the nature of the interlayer cation,[28] some chemical control of interface properties may be anticipated.

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[16] The amount of water added was calculated based on the total number of reactive protons that would have been provided by HF on a 1:1 mol basis.

[17] The H_2O_2 and HF solutions were added at 0.67 mL/min. The 1:1 Mg:Si solution was added from an addition funnel at 1 drop/s.

[18] Anal. Found (calcd. for $KMg_3Si_3AlO_{10}F_2$): 11.1% K_2O (11.18); 12.5% Al_2O_3 (12.10); 29.2% MgO (28.70); 42.7% SiO_2 (42.79); 8.68% F (9.02).

[19] Bloss, F. D.; Gibbs, G. V.; Cummings, D. *J. Geol.* **1963**, *71*, 537.

[20] Yvon, K.; Jeitschko, W.; Parthe, E. *J. Appl. Crystallogr.* **1977**, *10*, 73–74.

[21] Tarte, D. *Spectrochim. Acta* **1963**, *19*, 25–47.

[22] Engelhardt, G.; Michel, D. *High Resolution Solid State NMR of Silicates and Zeolites*; John Wiley and Sons, Ltd.: Chichester, 1987; p 485.

[23] Herrero, C. P.; Sanz, J.; Serratosa, J. M. *J. Phys. C.* **1985**, *18*, 13–22.

[24] Grimmer, A.-R.; Lampe, F. V.; Magi, M.; Lippmaa, E. *Z. Chem.* **1983**, *23*, 342.

[25] The films were assumed to be thin enough not to require treatment with H_2O_2 to remove carbonaceous products prior to calcination. Furthermore, evolution of gases, associated with H_2O_2 reactions would probably disrupt the film.

[26] McKernan, S.; Tsai, T.-L.; Carter, C. B.; Duldulao, F. D.; Burlitch, J. M. 93rd Annual Meeting of the Amer. Ceram. Soc.; Cincinnati, OH, 1991; Abstr. No. 2JIX-91.

[27] The 1:1 Mg:Si solution was mixed with enough MPA solution to make a precursor with 3 $Mg(OMe)_2$, 3 TEOS, 1 $Al(OBu^s)_3$, 1 K and 1 acacH.

[28] *X-ray Identification and Structures of Clay Minerals*; Brindley, G. W., Ed.; The Mineralogical Society: London, 1951; p 4.

Acknowledgment. We are grateful to the Office of Naval Research and DARPA for financial support and to the NSF (CHE7904825; PGM8018643), NIH (RR02002) and IBM Corp. for helping to provide NMR facilities in the Department of Chemistry. We acknowledge many helpful discussions with our collaborators, Dr. Kenneth Chyung and Dr. Steven Dawes of Corning, Inc., and Prof. C. Barry Carter and Prof. David Kohlstedt.

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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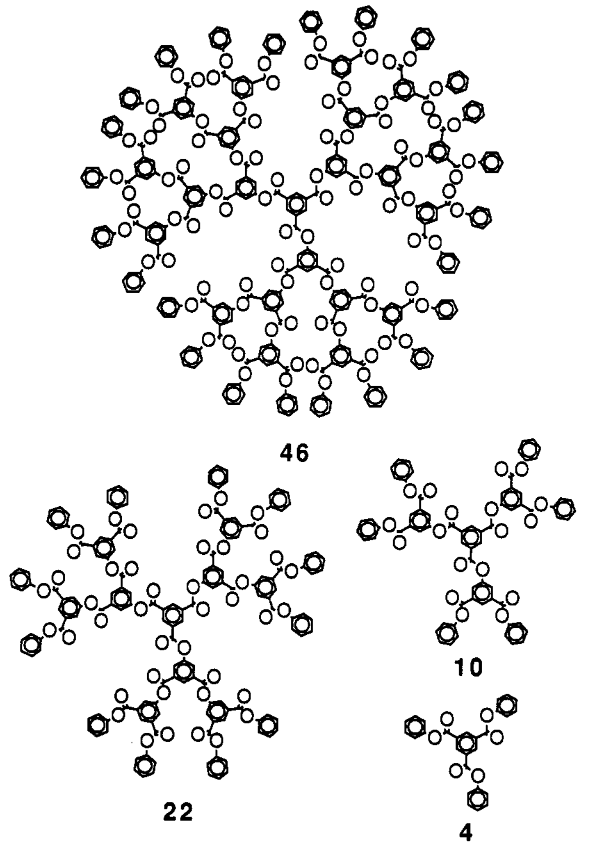
We describe here the convergent synthesis of a new family of starburst dendrimers based upon 1,3,5-linked aryl esters. Starburst polymers differ from conventional linear polymers in that each monomer unit except for the terminal units is a branch point. The original route to starburst dendrimers is divergent 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



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22

10

4

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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(1) (a) Tomalia, D. A.; Naylor, A. M.; Goddard III, W. A. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 138. (b) Tomalia, D. A.; Hedstrand, D. M.; Wilson, L. P. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1990; Index Vol., p 56.

(2) Hall, H. K.; Polis, D. W. *Polym. Bull.* **1987**, *17*, 409.

(3) Newkome, G. R.; Yao, Z.-q.; Baker, G. R.; Gupta, V. K.; Russo, P. S.; Saunders, M. M. *J. Am. Chem. Soc.* **1986**, *108*, 849.

(4) Miller, T. M.; Neenan, T. X. *Chem. Mater.* **1990**, *2*, 346.

(5) Hawker, C. J.; Frechet, J. M. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1010.

(6) Hawker, C. J.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.

(7) Hawker, C. J.; Frechet, J. M. J. *Macromolecules* **1990**, *232*, 4726.

(8) Washington, G.; Kwock, E. W.; Neenan, T. X.; Miller, T. M. Unpublished results.