acetate:hexane for **1a** and 1:2 ethyl acetate:hexane for **1b**). For **1a** the first band eluted is the desired product (isolated yield 75%) while the desired product is the second band for **1b** (isolated yield 65%).[8] The products are stable in air at room temperature in the solid state and in solution.

Cyclic voltammograms for the monomers in CH_3CN [0.1 M Bu_4NClO_4 (TBAP)] show a quasi-reversible ferrocene/ferricinium (Fc/Fc^+) couple and an irreversible amine oxidation process,[10] Table I and Figure 1a. For **1b** the onset voltage for electropolymerization occurs *negatively* of the Fc/Fc^+ couple precluding assignment of an $E°$ for this complex. However, compound **1e** does not electropolymerize, and due to their similarity we assume that complexes **1e** and **1b** have nearly the same $E°$.

Upon continuous potential cycling between 0 and 1.0 V at 20 mV/s in a rigorously deaerated electrolysis solution of **1a**, an adherent polymer film of the ferrocene complex deposits on the Pt electrode surface (Figure 1b). The monotonic increase in both i_{ox} and i_{red} for the Fc/Fc^+ couple clearly indicates polymer film formation. The reduction process marked with an asterisk in Figure 1b likely arises from an amine coupling product.[10] In the case of **1b** oxidation of the aromatic amine and film deposition occur under less forcing conditions than required for **1a**, $E_{ox,amine} = 0.41$ V (Figure 1c), and deaerating the solution is not necessary.

Neither complex **1c** nor **1d** electropolymerizes under any conditions investigated since the head (amine nitrogen) to tail (para position of an adjacent benzene ring) coupling sites expected for polymerization are blocked by steric bulk, **1c**, and site occupation, **1d**. These observations strongly suggest that head-to-tail coupling of the amines constitute the polymer backbone for the ferrocene polymer.[9,10] Support for the head-to-tail coupling also comes from infrared (IR) specular reflectance data taken on a poly-**1a**-coated Pt electrode for which only a very weak N–H absorption ($\nu_{N-H} = 3365$ cm^{-1}) is observed (Figure 3a). For poly-**1b** polymerization most likely occurs by coupling of the primary amine nitrogen to the 4 and/or 6 position, both of which are resonance-stabilized radical cations, on an adjacent benzene ring. IR specular reflectance measurements indicate the presence of ($\nu_{N-H} = 3370$ cm^{-1}) secondary amine functionalities in poly-**1b** films and possibly also some primary amine groups (shoulder at ~3450 cm^{-1}, Figure 3b). The relatively simple IR spectra observed for both polymers are somewhat unexpected, although other ferrocene polymer films also have simple IR spectra.[2c,4b,11]

When electrodes of either poly-**1a** or poly-**1b** are transferred to a solution containing only supporting electrolyte (0.1 M TBAP in CH_3CN) and scanned between 0 and 0.75 V, the voltammetric responses shown in Figure 2 are obtained (Table I). Voltage excursions more positive (1.25 V) and negative (−2.0 V, N_2 atmosphere) do not degrade the films. For thin films of either polymer examined at 5 mV/s sweep rate, the peak splitting, ΔE_p, the peak width at half-height, E_{fwhm}, can be as low as 10 and 110 mV respectively. Both quantities approach the theoretical values of 0 V and 90.5 mV for ΔE_p and E_{fwhm}, respectively, for a surface-confined species.[1a,12] Thicker films and faster scan rates (>50 mV/s) result in both increased peak splittings and peak widths, but the nearly symmetrical wave shape observed for the Fc/Fc^+ couple is maintained even at 200 mV/s. Thus the voltammetry for the Fc/Fc^+ portion of these polymer films is comparable to that for poly(vinylferrocene). No obvious redox processes for the "polyaniline" backbone are detected for either polymer film.[10] Poly-**1b** shows a broad, weak feature at 0.5–0.6 V, which has been observed in thick films of other ferrocene derivatives.[2,3] In 1 M H_2SO_4, poly-**1a** shows only modified voltammetry for the ferrocene portion,[1a] while poly-**1b** is unstable under these conditions and appears to "dissolve" off the electrode surface. Studies are ongoing to determine if voltammetry for the polyaniline backbone can be observed under other conditions.

A linear relationship holds for apparent surface coverage, Γ_{app},[13] as a function of the number of polymerization scans employed to grow the film (insert in Figure 2). Γ_{app} also is independent of scan rate between 2 and 50 mV/s for thin films, demonstrating a reasonably high charge-transport rate through the polymer. However, at high scan rates the measured Γ_{app} is less than predicted from slow scan rate data.

The ease of preparation, rapid polymerization rates, and electrochemical stability [less than 5% degradation in the measured oxidative and reductive currents (50 repetitive potential cycles (0–0.75 V vs SSCE at 50 mV/s))] make these polyaniline-based ferrocene polymers potentially useful for practical applications. We are exploring the generality of the reaction shown in eq 1 to prepare new complexes for use in polymer-modified electrodes.

Acknowledgment. This work was supported in part by the Defense Advanced Research Projects Agency through a grant monitored by the Office of Naval Research.

Registry No. **1a** (homopolymer), 127356-79-0; **1b** (homopolymer), 127356-80-3.

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[8] Anal. for **1a** calcd (found), $C_{17}H_{17}FeN$: C, 70.1 (69.96); H, 5.84 (5.84); N, 4.81 (4.44). ^1H NMR (**1a**, $CDCl_3$) δ 7.2–7.1 (m, 2 H), 6.7–6.6 (m, 3 H), 4.24 (tr, $J = 1.8$ Hz, 2 H), 4.17 (s, 5 H), 4.1 (tr, $J = 1.8$, Hz, 2 H), 3.99 (s, 7 H), 2.19 (br, 1 H). Anal. for **1b** calcd (found), $C_{17}H_{18}FeN_2$: C, 66.7 (66.20); H, 5.88 (5.86); N, 9.15 (8.76). ^1H NMR (**1b**, $CDCl_3$) δ 7.0 (tr, $J = 7.9$ Hz, 1 H), 6.0–6.15 (m, 3 H), 4.25 (tr, $J = 1.9$ Hz, 2 H), 4.2 (s, 5 H), 4.16 (tr, $J = 1.9$ Hz, 2 H), 3.94 (s, 2 H); 3.65 (br, 3 H).

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[10] (a) Wei, Y.; Focke, W. W.; Wnek, G. E.; Ray, A.; MacDiarmid, A. G. *J. Phys. Chem.* **1989**, *93*, 495. (b) Wnek, G. E. *Synth. Met.* **1986**, *15*, 213.

[11] Electrolysis of either poly-**1a** or poly-**1b** at 0.75 V vs SSCE in 0.1 M TBAP containing ~0.05 M 2,2′-bipyridine (bpy) results in the formation of $[Fe(bpy)_3]^{3+}$ as identified by its UV–vis spectrum and a red solution. These experiments confirm the presence of iron in both polymers.

[12] Bard, A. J.; Faulkner, L. F. *Electrochemical Methods*; Wiley: New York, 1980.

[13] Γ_{app} determined from the equation $\Gamma_{app} = Q/(nFA)$, where Q is the charge (area) under the oxidative wave, n is the number of electrons per metal site ($n = 1$), F is Faraday's constant, and A is electrode area ($A = 0.15$ cm^2).

Convergent Synthesis of Monodisperse Dendrimers Based upon 1,3,5-Trisubstituted Benzenes

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A growing area of materials chemistry deals with the synthesis and properties of organic structures with specific molecular architectures, including molecular rods,[1]

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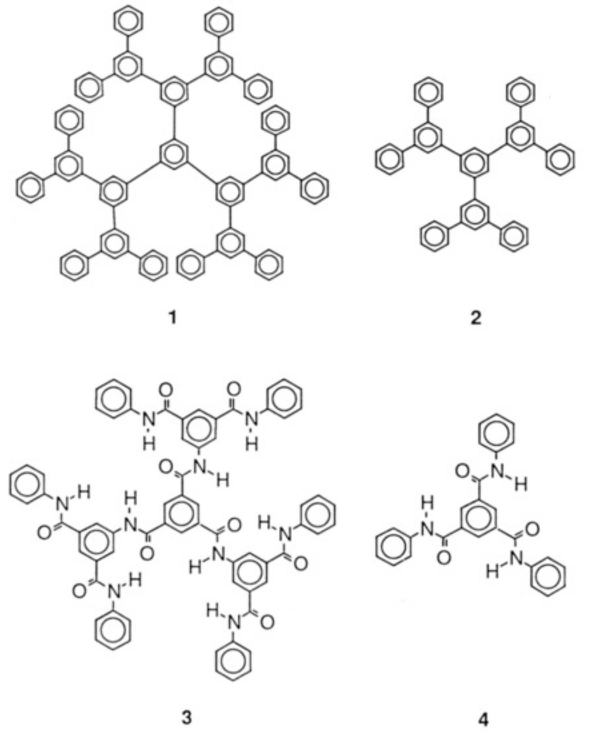
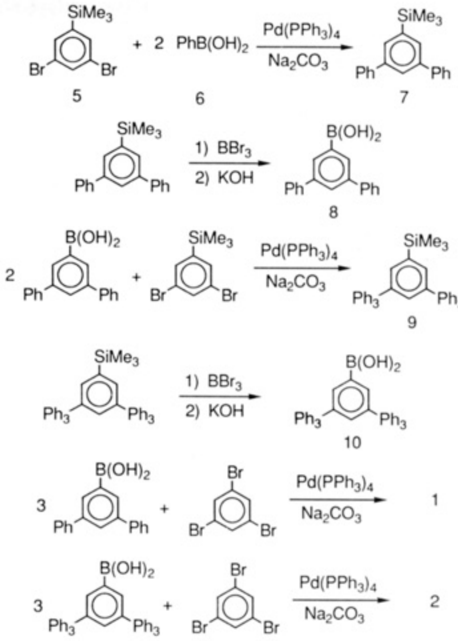
Figure 1. Space filling molecular model of **1**.

Scheme I



Scheme II



spheres,[2] and cubes.[3] Possible applications of materials of this type include novel molecular building blocks for nanotechnology,[4] molecular weight or size standards,[5] or X-ray beam scattering materials. We describe here a new, simple, convergent synthetic approach to the construction of large organic spheres based upon 1,3,5-triarylbenzenes and 1,3,5-triarylamides. Prototypical of these materials is **1** (Figure 1, Scheme I), consisting of 22 phenyl rings joined symmetrically and whose molecular structure approximates a sphere.[6] Compound **1** and the smaller molecular sphere **2**, consisting of 10 phenyl rings joined in the same fashion, are easily prepared in gram quantities, have thermal stabilities >350 °C in air, and are the first examples of entirely aromatic analogues of starburst dendrimers described by Tomalia.[7] The distinguishing feature of our synthesis of **1** and **2** is that the final step involves coupling of preformed dendrons with a molecular core. This convergent approach permits simple purification of the products, since partially formed dendrimers having fewer than three dendrons are easily distinguishable chromatographically from **1** and **2**. In this way we can prepare large monodisperse molecular dendrimers having well-defined architecture and diameters of >20 Å. Initial results on an analogous system consisting of phenyl rings joined sym-

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(1) (a) Kaszynski, P.; Michl, J. *J. Am. Chem. Soc.* **1988**, *110*, 5225. (b) Murthy, G. S.; Hassenruck, K.; Lynch, V. M.; Michl, J. *J. Am. Chem. Soc.* **1989**, *111*, 7262.

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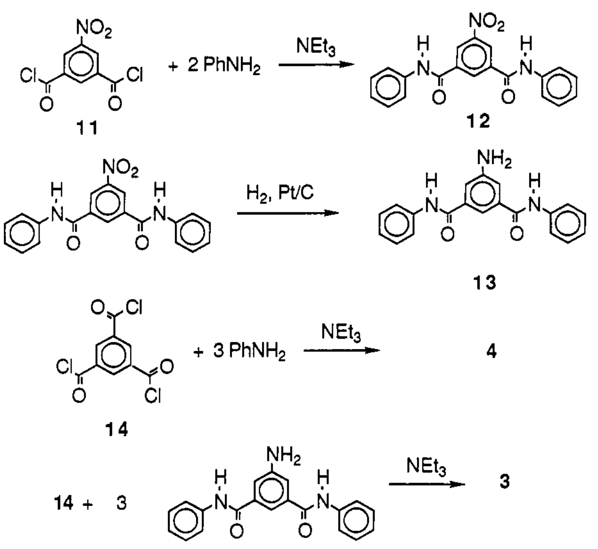
(6) These dendrimers possess spherelike morphology as defined by space-filling models of the polyaryls described in this communication. There is however no reason why analogous materials such as molecular cubes, pyramids, or other architectures could not be prepared by a judicious choice of building blocks. Tomalia has defined the term starburst dendrimers for materials prepared by him consisting of radially symmetrical three-dimensional molecules based upon concentric tiers of β-carbomethoxyethyl or β-alanine units symmetrically branched through their terminal nitrogens. Starburst dendrimers may approach monodispersity but are not necessarily defined to be monodisperse. Because of our particular synthetic approach, our starburst dendrimers are monodisperse.

(7) For an excellent overview of developments in starburst dendrimers see ref 2. (a) See also: Naylor, A. M.; Goddard III, W. A.; Kiefer, G. E.; Tomalia, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2339. (b) Tomalia, D. A.; Hall, M.; Hedstrand, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 1601. (c) Tomalia, D. A.; Baker, H.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Smith, P. *Polym. J. (Tokyo)* **1985**, *17*, 117. (d) Tomalia, D. A.; Baker, H.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Smith, P. *Macromolecules* **1986**, *19*, 2466. (e) Tomalia, D. A.; Berry, V.; Hall, M.; Hedstrand, D. M. *Macromolecules* **1987**, *20*, 1167.

Scheme III



metrically by amide linkages are also reported here. Other workers[2,7-10] have described *divergent* approaches to starburst and other highly branched molecules in which successive generations are formed by coupling geometrically increasing numbers of repeat units to the outer surface of the growing dendrimer.

The synthesis of the dendrimers 1 and 2 involves reaction of the readily obtained 3,5-dibromo-1-(trimethylsilyl)benzene,[11] 5, with phenylboronic acid, 6, under the coupling conditions developed by Suzuki (Scheme II).[12] Reaction of 3,5-diphenyl-1-(trimethylsilyl)benzene, 7, with boron tribromide[13] and hydrolysis of the resulting arylboron dibromide with aqueous base yield the new arylboronic acid 8. In the same way, 8 may be reacted once again with 5, and through the intermediacy of 9 an arylboronic acid, 10, having seven phenyl rings may be prepared. Coupling of these dendrimers with 1,3,5-tribromobenzene, 12, in refluxing toluene/ethanol or toluene/tetrahydrofuran takes place in approximately 1 day. The progress of the reactions, even for the synthesis of 1, is easily monitored by thin-layer chromatography. Compounds 1 and 2 are purified by conventional column chromatography, followed by recrystallization, and are isolated as white microcrystalline materials in yields of 31 and 29% (based on 5), respectively.[14] Compounds 1 and 2 show remarkable solubility in common organic solvents such as chloroform, carbon tetrachloride, or toluene. The solubility of 1 in toluene is 120 mg/mL. Space-filling molecular models indicate that the approximate diameters for the materials described in this communication are 20 and 21 Å for 1 and 3, respectively.

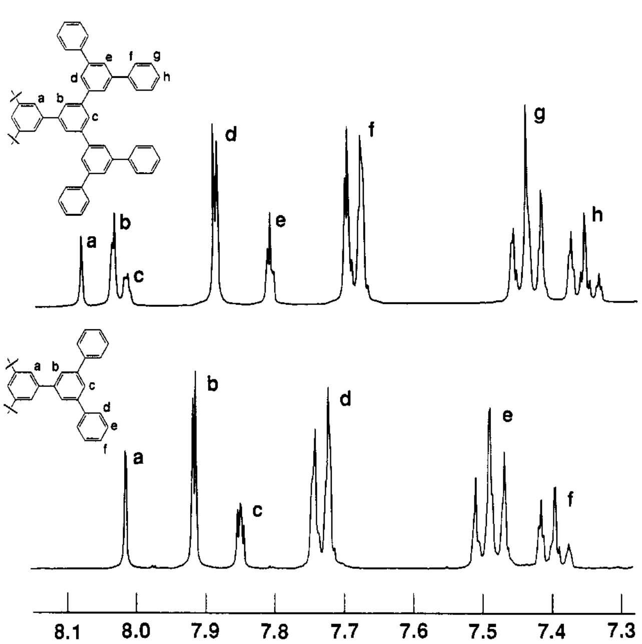


Figure 2. ^1H NMR spectra of 1 and 2 in $CDCl_3$ at 360 MHz.

The synthesis of materials based upon aryl amides 3 and 4 follows the same general approach (Scheme III). The simplest example, 4, was prepared by the reaction of 3 equiv of aniline with 1,3,5-benzenetricarbonyl trichloride, 14, in the presence of triethylamine. For the synthesis of the 10 phenyl ring amide, compound 3, 2 equiv of aniline was allowed to react with 1-nitro-3,5-benzenedicarbonyl dichloride, 11. Reduction of the nitro group (H_2 over Pt/C) followed by reaction of the new arylamine 13 with 1,3,5-benzenetricarbonyl trichloride yielded 3. We are currently extending this synthetic scheme to the synthesis of larger amide-based dendrimers.

The structures of compounds 1–4 were confirmed by a combination of ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis.[15] The high symmetry of 1–4 renders ^1H NMR spectroscopy particularly useful in their characterization. At 360 MHz, every proton resonance is distinguishable and assignable in all four compounds. Protons nearer the interior of 1 and 2 resonate farther downfield than protons further from the interior

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(8) Recent work describes the polymerization of 3,5-dibromophenylboronic acid using catatylic amounts of Pd(0). This reaction yields polyphenyls of the same general type as we describe in this report but with a broad molecular weight distribution (D = 1.26–2.02) and with varying amounts of terminal bromine and boronic acid groups. Kim, Y. H.; Webster, O. W. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1988**, *29*, 310. (b) Kim, Y. H.; Webster, O. W. *J. Am. Chem. Soc.* **1990**, *112*, 4592.

(9) There has also been a report of low molecular weight starburst dendrimer materials based upon polyarylamines using a protect/deprotect scheme with 2,4-dinitrofluorobenzene as the starting material. Hall, H. K.; Polis, D. W. *Polym. Bull.* **1987**, *17*, 409.

(10) A related, interesting system involves the divergent synthesis of molecules termed arborols. Newkome, G. R.; Yao, Z.-q.; Baker, G. R.; Gupta, V. K.; Russo, P. S.; Saunders, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 849.

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(13) Haubold, W.; Herdtle, J.; Gollinger, W.; Einholz, W. *J. Organomet. Chem.* **1986**, *315*, 1.

(14) We have succeeded in growing large single crystals of compound 2. A crystallographic study will be the subject of a future report.

(15) Compound 1, 1,1′:3′,1″:3″,1‴:3‴,1⁗:3⁗,1′′′′′:3′′′′′,1′′′′′′-septiphenyl, 5‴-(5′,5‴-diphenyl[1,1′:3′,1″:3″,1‴:3‴,1⁗-quinquephenyl]-5″-yl)-5′,5′′′′′-diphenyl-5″,5⁗-bis([1,1′:3′1″-terphenyl]-5′-yl)-: mp 342–347 °C; ^1H NMR ($CDCl_3$) 8.07 (s, 3 H), 8.02–8.04 (m, 6 H), 7.99–8.02 (m, 3 H), 7.88 (d, 1.4 Hz, 12 H), 7.80 (t, 1.4 Hz, 6 H), 7.65–7.70 (m, 24 H), 7.40–7.45 (m, 24 H), 7.32–7.38 (m, 12 H) ppm. ^{13}C NMR ($CDCl_3$) 142.79, 142.74, 142.54, 142.07, 140.99, 128.83, 127.56, 127.38, 126.27, 126.00, 125.91, 125.58, 125.38 ppm. Anal. Calcd for $C_{132}H_{90}$: C, 94.59; H, 5.41. Found: C, 94.78; H, 5.44. Compound 2, 1,1′:3′,1″:3″,1‴:3‴,1⁗-quinquephenyl, 5′,5‴-diphenyl-5″-[1,1′:3′,1″-terphenyl]-5′-yl-: mp 272–274 °C; ^1H NMR ($CDCl_3$) 8.01 (s, 3 H), 7.91 (d, 1.4 Hz, 6 H), 7.85 (t, 1.4 Hz, 3 H), 7.71–7.74 (m, 12 H), 7.46–7.51 (m, 12 H), 7.36–7.42 (m, 6 H) ppm. ^{13}C NMR ($CDCl_3$) 142.65, 142.57, 142.19, 128.87, 127.61, 127.42, 125.85, 125.85, 125.61, 125.40 ppm. Anal. Calcd for $C_{60}H_{42}$: C, 94.45; H, 5.55. Found: C, 94.14; H, 5.51. Compound 3, 1,3,5-benzenetricarboxamide, *N,N′,N″*-tris[3,5-bis[(phenylamino)carboxyl]phenyl]-: mp 295–309 °C. ^1H NMR (DMSO-d_6) 11.06 (s, 3 H), 10.53 (s, 6 H), 8.92 (s, 3 H), 8.62 (s, 6 H), 8.36 (s, 3 H), 7.79–7.85 (m, 12 H), 7.35–7.43 (m, 12 H), 7.09–7.17 (m, 6 H) ppm. ^{13}C NMR (DMSO-d_6) 165.1, 164.7, 139.4, 129.1, 138.0, 135.9, 135.1, 128.7, 123.9, 122.6, 122.0, 120.3 ppm. Anal. Calcd for $C_{69}H_{51}N_9O_9 \cdot 1.6H_2O$: C, 70.28; H, 4.64; N, 10.69. Found: C, 70.28; H, 4.83; N, 10.80. Compound 4, 1,3,5-benzenetricarboxamide, *N,N′,N″*-triphenyl-: mp 317–321 °C; ^1H NMR (THF-d_8) 9.83 (s, 3 H), 8.68 (s, 3 H), 7.80–7.86 (m, 6 H), 7.27–7.34 (m, 6 H), 7.04–7.10 (m, 3 H) ppm. ^{13}C NMR (THF-d_8) 165.2, 140.4, 140.3, 137.2, 130.0, 129.4, 125.9, 124.6, 121.0 ppm. Anal. Calcd for $C_{27}H_{21}N_3O_3$: C, 74.47; H, 9.86; N, 9.65. Found: C, 74.14; H, 9.98; N, 9.61.

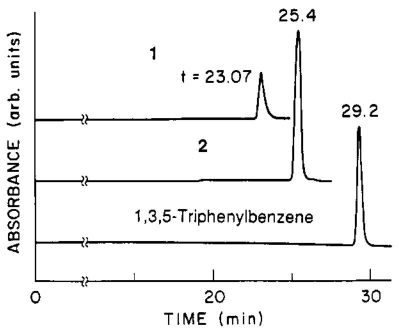

Figure 3. Gel permeation chromatograms of dendrimers 1, 2, and 1,3,5-triphenylbenzene.

(Figure 2).[16] Gel permeation chromatography of 1–4 resulted in a single peak for each with polydispersity below the resolution limit of the technique (Figure 3). The UV spectra of **1** and **2** showed broad maxima centered at 260 nm with extinction coefficients of 1.41 × 10^5 and 3.63 × 10^5 M^{-1} cm^{-1}. The UV spectra and the absence of color in **1** and **2** indicate that 1,3,5-triphenylbenzene is a good model for the chromophore in **1** and **2**.

Mass spectra of the dendrimers **1**, **2**, and **4** (fast atom bombardment) show clean parent ions for each compound. The dendrimers **1**–**4** are thermally stable (>350 °C in air) and, unlike dendrimers based upon alkyl amides, do not discolor or aggregate upon standing in solution.[17] This stability may be an important factor in developing applications for these materials as for , e.g., X-ray beam calibration standards. We are actively pursuing our investigations of these materials and other larger aromatic dendrimers in which phenyl rings are separated by amide, ester, and acetylenic units. Results of these approaches will be the subject of future reports.

Acknowledgment. We acknowledge helpful discussions with E. A. Chandross and thank Elizabeth W. Kwock for gel permeation chromatographic data.

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[16] This supports the notion of a branch cell hierarchy as described in ref 2.

[17] Starburst dendrimers based upon poly(alkylamides) have recently become commercially available from Polysciences, Warrington, PA, under license from The Dow Chemical Co. The accompanying literature recommends storing the materials under an atmosphere of nitrogen, at 4 °C, and at pH close to 7. Deviations from these conditions are reported to lead to discoloration and aggregation of materials.

Electrically Conductive Polymer–Ultra-High-Modulus Polymer Alloys. A Solution Processing Route to Hybrid Fibers of Kevlar–Polypyrrole

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An attractive approach to enhancing the mechanical properties, environmental stability, processability, and other desirable characteristics of electrically conductive polymers[1] is to prepare hybrid materials in which they are "alloyed" with polymers having complementary properties.[2] In the case of polypyrrole,[1,3] composite films have been prepared electrochemically on a small scale with poly(vinyl alcohol),[4] poly(vinyl chloride),[5] polyurethane,[6] and polystyrene.[7] Although such materials have useful characteristics, it would also be of great interest to prepare polypyrrole alloys with fiber-forming ultrahigh-modulus polymers such as poly(*p*-phenyleneterephthalamide) (PPTA, Kevlar).[8] However, the intractability of conventional polypyrrole,[3,9] and the traditional approach of processing of PPTA from strong acids[8,10] present a serious obstacle. In this communication, we report a successful route to PPTA–polypyrrole hybrid fibers[11] that capitalizes upon the high solubility of N-metalated PPTA[12] and pyrrole in polar organic solvents.

Table I. Properties of PPTA–Polypyrrole Fibers

spin-draw ratio	diameter, μm	polypyrrole content,[a] wt %	σ(300 K), S/cm
1.0[b]	220	59.2	7.7
1.3	74	57.2	0.6

[a] From elemental analysis. See footnote 17 for data. [b] A takeup drum was not employed.

In a typical preparation, distilled pyrrole (50–80 wt % of the final solution) was added to a dry DMSO solution of *N*-NaPPTA,[13] and the resulting red solution was stirred at room temperature under inert atmosphere. It was noted that the viscosity of the solution decreases markedly upon addition of pyrrole. This may arise from *N*-NaPPTA carbonyl group–pyrrole hydrogen bonding and/or partial

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