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Architectural Copolymers: Rod-Shaped, Cylindrical Dendrimers

R. Yin, Y. Zhu, and D. A. Tomalia*

Michigan Molecular Institute
1910 W. St. Andrews Road
Midland, Michigan 48640

H. Ibuki

Biochemistry Department, Unitika Ltd. R&D Center
23 Kozakura, Uji, Kyoto, 611 Japan

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Rodlike, cylindrical dendrimers were first synthesized by divergent strategies as early as 1987;[1,2] however, inadequate analytical methodology precluded unequivocal characterization until now. Recent seminal reports by Percec[3] have described the "quasi-equivalence" of dendrons as a function of backbone degree of polymerization (N_c) (see Figure 1B for dendrons at lower generation levels (i.e., $G = 1$ or 2)). Percec et al. have clearly demonstrated that they can induce polymeric shape control from spheroids to cylindrical polymers as a function of backbone multiplicity N_c. Related work by Schlüter[4] has shown that polymerizable monodendrons or dendronization of polymeric backbones lead to the formation of cylindrical dendrimers; however, unequivocal characterization has been hampered by their strong propensities to undergo aggregation.

We now report the first divergent synthesis of rod-shaped, cylindrical dendrimers derived from a high multiplicity (N_c = 100−500), linear, random coil polymeric core (Figure 1B) and their transformation from random coil to extended cylindrical conformations as a function of generation level enhancement. Since our first work on poly(amidoamine) (PAMAM) dendrimers in the early 1980s,[5] attention has focused almost exclusively on low multiplicity (N_c = 1−6) pointlike cores leading to substantially spheroidal morphologies,[3e,6,7] illustrated by the dendritic structural/mathematical notation (Figure 1A). From notation B, it can be readily visualized that the aspect ratios of these dendrimers may be controlled as a function of the dendron generation level (G) and the polymerization degree (N_c) of the linear core. As the generation level increases, amplification of dendron structure along the linear core chain forces tethered congestion until chain extension is attained at $G = 4$. These dendrimer hybrids represent a new "hybridized macromolecular topology", which we refer to as *architectural copolymers*. They are copolymers derived from a combination of linear and dendritic macromolecular architectures.[8]

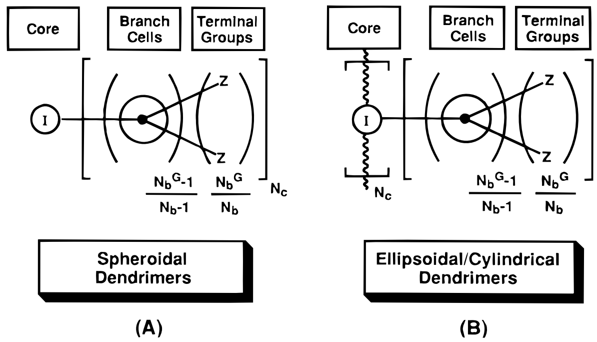

Figure 1. (A) Structural notation for spheroidal dendrimers. (B) Structural notation for ellipsoidal/cylindrical dendrimers. N_c = core multiplicity; N_b = branch cell multiplicity; G = generation.

Appropriate initiator cores were synthesized by the living cationic polymerization of 2-ethyl-2-oxazoline with methyl tosylate as initiator. Subsequent deprotection by acid hydrolysis produces a reactive poly(ethyleneimine) (PEI) core with an identical N_c, typically ranging from 100 to 500 (DP = N_c = 100−500). This linear-PEI core synthesis is identical to those described earlier for constructing dendrigraft architectures.[9] Dendronization of these *l*-PEI's was performed using "*divergent, in situ branch cell*" synthesis strategies[10] which were adapted to the reaction sequence illustrated in Scheme 1. It was necessary to use substantially larger excesses of ethylenediamine (1260−10000 mol/ester group) at the amidation stage with longer reaction times (5−8 days, 5 °C) to ensure completion. Failure to follow these criteria led to polydispersed or insoluble, cross-linked products. Despite this modified synthesis, long-term storage (>2−3 months at 25 °C) of these dendrimers in the neat amine-terminated form occasionally led to sporadic cross-linked products. Conversion to sodium carboxylated terminal groups by alkaline hydrolysis provided products which were pacified and remained soluble even after long-term storage (i.e., >6 months). The products were generally isolated as white-cream solids and characterized by FTIR, ^{13}C NMR, SEC, HPLC, MALDI-TOF MS, and transmission electron microscopy (TEM).

Examination by TEM of the high multiplicity core (N_c = 350−500) dendrimers functionalized with sodium carboxylate surfaces revealed unique morphogenesis patterns as a function of generation level. High sodium atom densities at the periphery of the dendrimer surfaces allowed direct imaging without the need for conventional staining, as we have reported earlier.[10] Lower generation dendrimers gave TEM images ranging from nondescript blobs (G = 0 and 1; Z = CO_2Na) to somewhat elongated

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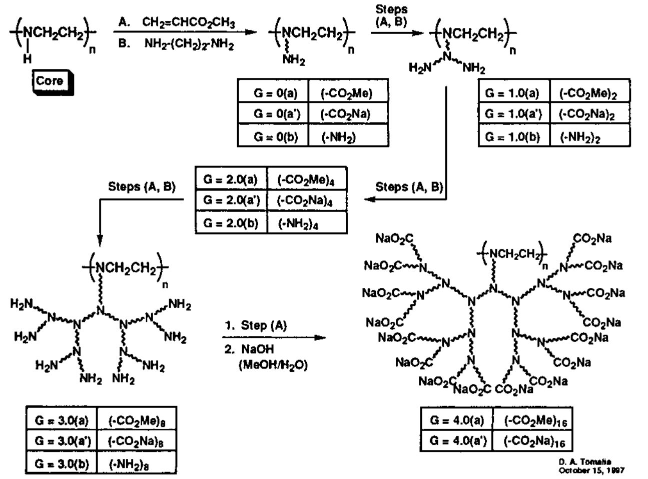
Scheme 1. Dendronization Scheme for Conversion of Linear Poly(ethyleneimine) Cores to Dendri Poly(amidoamine) Hybrids



nonspherical clusters ($G = 2-3$; Z = CO_2Na) reminiscent of random coil conformations. *At the ($G = 4$; Z = CO_2Na) stage, a remarkable molecular morphogenesis occurred.* As shown in Figure 2a extensions to elongated rods were observed throughout the hybrid dendrimer species population, accompanied by apparent self-organization into parallel bundles of extended rods. Individual rod diameters as measured from the electron micrograph appear to range between 25 and 32 Å. Preliminary molecular modeling experiments indicate individual rod diameters of approximately 35−45 Å. On the basis of the lengths of distinguishable individual rods (i.e., DP = 100−500), the lengths appear to range from ≅500−3000 Å. Thus, aspect ratios range from approximately 15 to 100 depending on the degree of polymerization of the linear poly(ethyleneimine) core used. It is of interest to compare these shapes and morphologies directly with the shapes and assemblies obtained for pointlike initiator core (NH_3) dendrimers possessing identical surface groups at the same generation level.[11] A related "molecular shape change" was reported by one of us (D.A.T.) as early as 1989 for dendrimers derived from pointlike cores. This molecular morphogenesis has been amply demonstrated by photochemical probe experiments[12] and occurs for PAMAM dendrimers (NH_3 core) between $G = 3$ and 4. Work is in progress to investigate the implications of these features in the present dendrimer rod systems. In summary, these new nanoscale dendritic morphologies add new options to the repertoire of known dendrimer building blocks for the controlled synthesis of higher ordered covalent complexity as well as the construction of nanoscale devices and modules.[13,14]

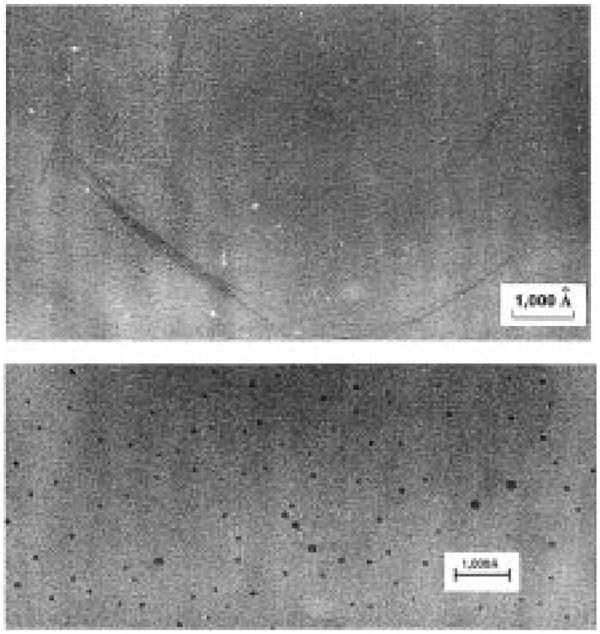


Figure 2. (a) Electron micrograph (TEM) of linear poly(ethyleneimine) (PEI) core; dendri poly(amidoamine) PAMAM; $G = 4$(a); Z = $(-CO_2Na)_{16}$; $N_c = 300-500$. *Note*: self-organization of dendrimer rods into parallel arrays. (b) Electron micrograph (TEM) of ammonia (NH_3) core; dendri poly(amidoamine) PAMAM; $G = 4$(a); Z = $(-CO_2Na)_{48}$; $N_c = 3$. *Note*: self-organization of dendrimer spheroids into clusters.

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Supporting Information Available: Details of the experimental procedures, characterization data and flowchart for dendronization steps ($G = 0-4$) are described (9 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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