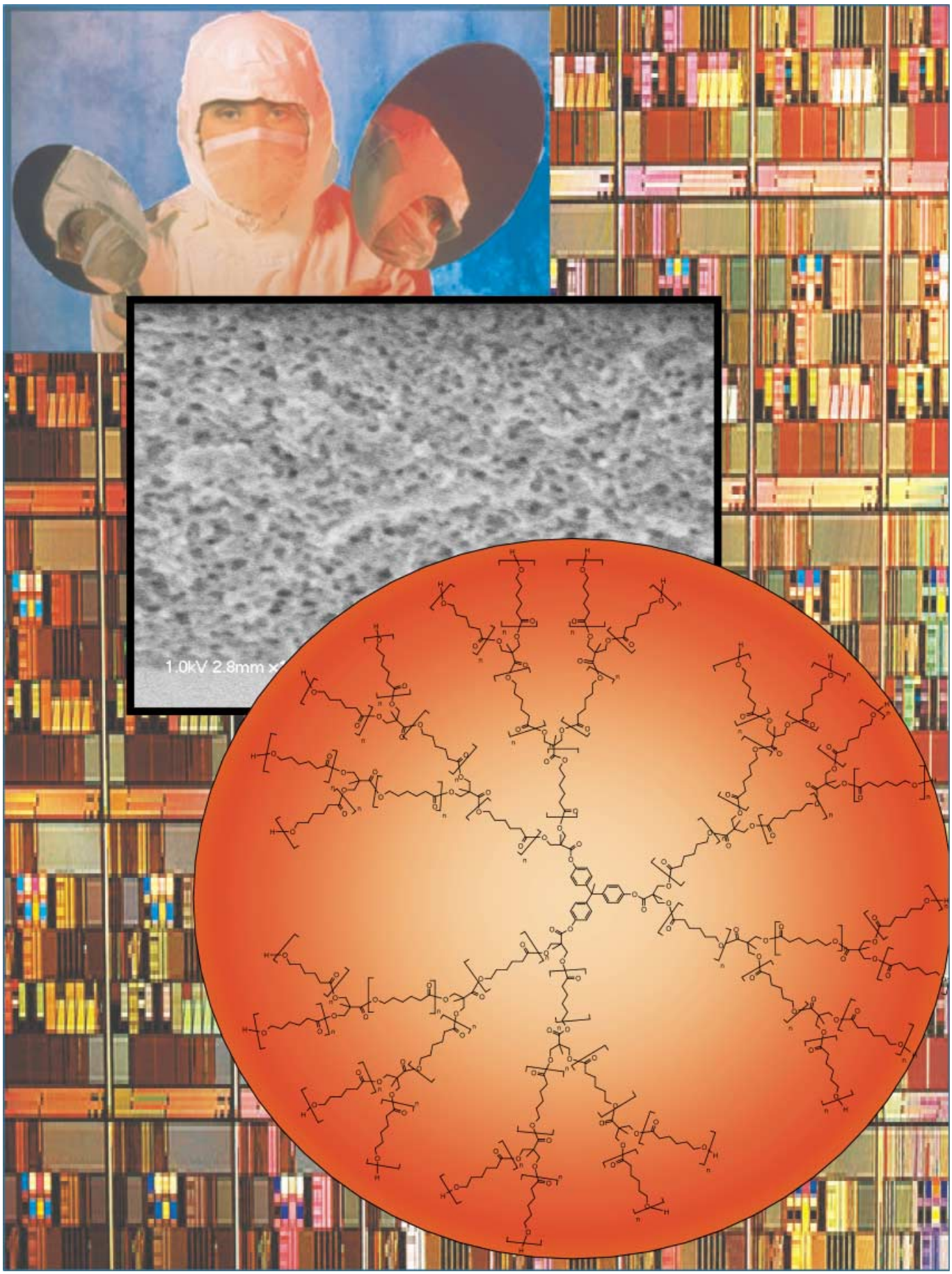

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Application of Complex Macromolecular Architectures for Advanced Microelectronic Materials

James L. Hedrick,* Teddie Magbitang, Eric F. Connor, Thierry Glauser, Willi Volksen, Craig J. Hawker, Victor Y. Lee, and Robert D. Miller[a]

Abstract: The distinctive features of well-defined, three-dimensional macromolecules with topologies designed to enhance solubility and amplify end-group functionality facilitated nanophase morphologies in mixtures with organosilicates and ultimately nanoporous organosilicate networks. Novel macromolecular architectures including dendritic and star-shaped polymers and organic nanoparticles were prepared by a modular approach from several libraries of building blocks including various generations of dendritic initiators and dendrons, selectively placed to amplify functionality and/or arm number, coupled with living polymerization techniques. Mixtures of an organosilicate and the macromolecular template were deposited, cured, and the phase separation of the organic component, organized the vitrifying organosilicate into nanostructures. Removal of the sacrificial macromolecular template, also denoted as porogen, by thermolysis, yielded the desired nanoporous organosilicate, and the size scale of phase separation was strongly dependent on the chain topology. These materials were designed for use as interlayer, ultra-low dielectric insulators for on-chip applications with dielectric constant values as low as 1.5. The porogen design, chemistry and role of polymer architecture on hybrid and pore morphology will be emphasized.

Keywords: living polymerization · macromolecular architectures · nanoporous organosilicates · nanostructures · organic nanoparticles

Introduction

For the past four decades, the semiconductor industry has experienced a two-fold increase in performance approximately every three years.[1] This increase in performance has historically been achieved by a reduction in device dimensions driven primarily by advances in microlithography, allowing on-chip device densities to continue to increase. Even though feature dimensions are projected to decrease to 100 nm or less in the foreseeable future, this alone may not be sufficient to continue the historic performance and density improvements. Clearly, revolutionary and innovative technologies are required to maintain the expected performance enhancements at these dimensions. The switch to copper metallurgy is one such example that resulted in a 10 to 20% increase in performance.[2] Silicon on insulator and silicon germanium are other more recent examples of materials breakthroughs that have significantly bolstered performance, which collectively, have minimized the deviation from the performance/density "treadmill".[3] The continual increase in device and wiring densities has placed increasing demands on the insulating material, which for IBM, has driven the switch from silicon oxide ($\kappa = 4.0$) to a high temperature thermosetting polyarylene ether with a dielectric constant of 2.6.[4] Future generations of chips will require dielectric constants below 2.0 to realize the full benefits of the reduced feature sizes.

Arguably the only route to a material that satisfies the stringent integration requirements with a dielectric constant below 2.0 is by the introduction of controlled porosity (i.e., a nanocomposite of an insulating material and air ($\kappa = 1.01$)) with pore sizes well below the smallest device features (≈ 100 Å or less required).[5] One approach to nanoporous organic materials utilizes the self-assembly of block copolymers, where one block is selectively removed to generate pores that are identical in size and shape to the initial block copolymer morphology.[6] Another set of materials that have attracted significant attention are silica aero- and xerogels produced by the sol–gel hydrolysis of orthosilicate esters followed by removal of solvents.[7] Alternatively, surfactants which self-assemble during the sol–gel vitrification can be used to ultimately produce well-ordered silica.[8] Since the dielectric constant of silica is ≈ 4.0, significant porosity (ca. 60%) is required to bring the dielectric constant below 2.0. Organosilicates, such as poly(silsesquioxanes) (SSQ), possess the requisite thermal and mechanical stability for microelectronic device fabrication,[9] and since the dielectric con-

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stant of the bulk material is only ≈2.8, modest levels of porosity will drive the dielectric constant below 2.0. The strategy employed to generate porosity uses a sacrificial macromolecular porogen which templates the SSQ vitrification into nanostructures and ultimately generates a porous structure upon thermolysis of the porogen. Since polymer mixtures typically undergo macroscopic phase separation, the successful preparation of hybrid materials with features in the nanometer regime, requires distinctive material properties. The unique features of functional,[10] dendritic[11, 12] and nanostructured[13] macromolecules distinguish them from their linear analogues.[14] These attributes have been exploited to accurately control phase separation in the hybrids.[10c, 15] The concept is shown is Figure 1 along with a FESEM micrograph of a porous SSQ. Mixtures of SSQ and the macromolecular template, in this case a star-shaped polycaprolactone, are deposited, cured and the phase separation of the organic component, organizes the vitrifying silicate into nanostructures.[5c] Removal of the sacrificial polymer by thermolysis yields the desired nanoporous organosilicate, and the pore size depends on the template architecture. As a class of materials, aliphatic polyesters were primarily investigated as porogens, since they degrade quantitatively in the appropriate temperature regime. This review will focus on the design and chemistry of several novel classes of branched and functional polyesters, including dendritic polymers, star-shaped polymers, dendritic-linear copolymers and organic nanoparticles, and the pronounced effect polymer architecture has on the hybrid and pore morphology.

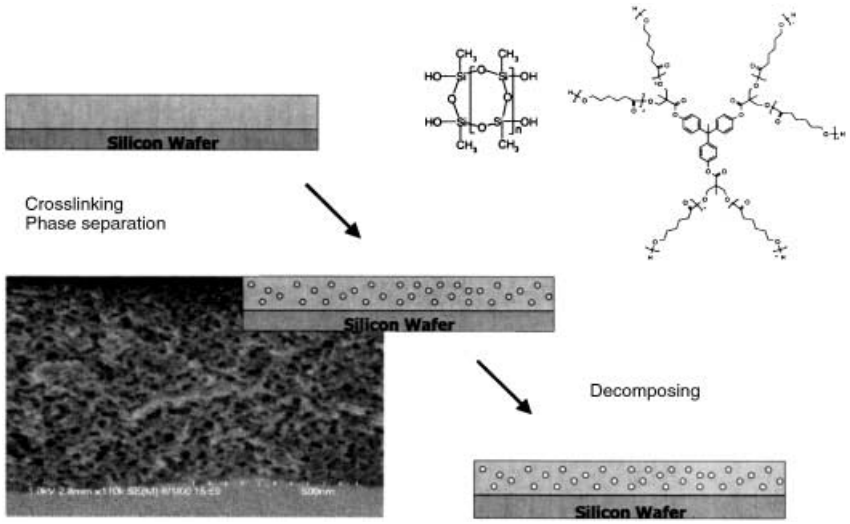

Figure 1. General approach to the formation of porous organosicates.

Dendritic Polymers

Dendritic-like star polymers, as a general class of macromolecules, are defined as branched materials having generations of high molecular weight polymer between branching junctures. These materials have comparable mechanical properties to their linear analogues, yet possess many features typical of dendrimers and hyperbranched polymers including advantageous solution and rheological properties and abundant chain end functionality. In contrast to dendrimers which require multiple synthetic transformations and associated purification steps to achieve modest molecular weights (≈5000 g mol^{-1}), molecular weights up to 250000 g mol^{-1} are possible in the dendritic polymers in just a few generations. Reports concerning the synthesis and characterization of these materials are much less pervasive when compared to dendrimer literature. Dendrigraft[16, 17] and comb-burst[18] architectures are among the most noteworthy examples of these dendritically branched linear or star macromolecules. These architectures are constructed by successive grafting of polymeric blocks. For example Gnanou et al.[19] prepared a branched poly(ethylene oxide) by iterative AB_2 functionalization and subsequent polymerization, while the hyperbranched analogue was reported in a one-step approach from an AB_2 macromonomer.[20] The driving force for investigating dendritic polymers as macromolecular templates for the generation of nanoporosity is two-fold. First and most importantly, in comparison to a dendrimer of comparable generation, the size of a dendritic polymer is larger and can be on the order of tens of nanometers. Secondly, the often overwhelming contributions of chain-end functionality of dendrimers is somewhat mediated once tethered onto short polymer chains. Comparison of an aliphatic polyester dendritic polymer composed of three generations of polycaprolactone and a dendrimer illustrates these points (Scheme 1).

We have explored a modular approach to the design and synthesis of dendritic polymers from libraries of multifunctional orthogonally protected initiators, functional dendrimers and dendrons all in tandem with living polymerization techniques. Derivatives of the compound 2,2-bis(hydroxymethyl) propionic acid (bis-MPA) served as both initiators and branching junctures, in the form of either dendrimers, dendrons or hyperbranched isomers using procedures developed by Hult[21] and others[22] for the construction of these complex architectures. This functionality provides exquisite markers for the spectroscopic analysis of the polymers, as the quartenary carbon and the protons on the methylene group are very sensitive to the substitution of the neighboring hydroxyl groups.[23] From the ^{1}H and ^{13}C NMR analyses, the efficiency of the initiation and the degree of branching can be obtained. The linear chains which comprise the generations are aliphatic polyesters prepared by the living ring-opening polymerization (ROP) of cyclic esters in the presence of stannous octanoate, $Sn(Oct)_2$. The coordination-insertion polymerization mechanism using $Sn(Oct)_2$ as the catalyst

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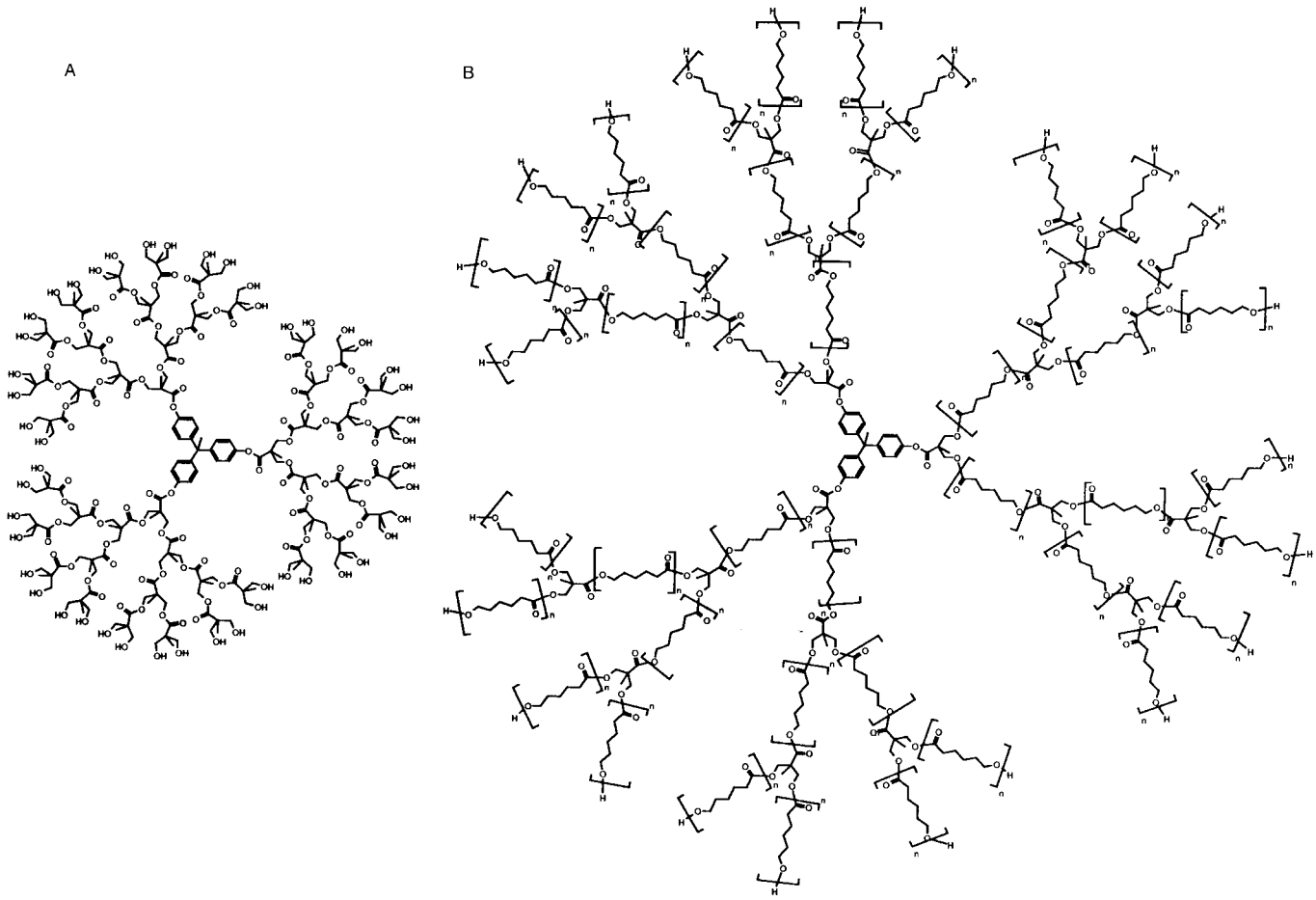
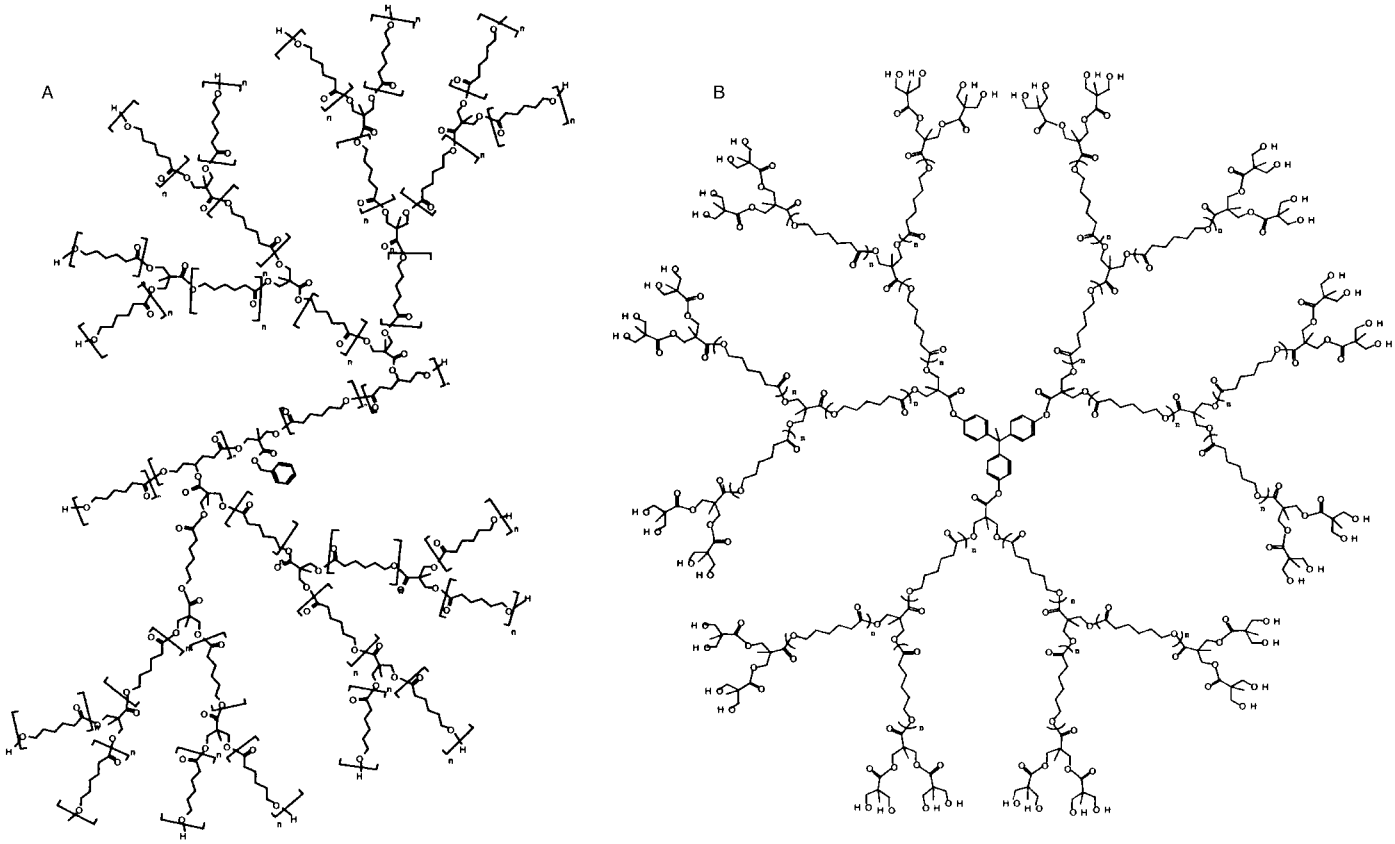


Scheme 1. Comparison of (A) aliphatic dendrimer to (B) dendritic-like star polymer.

with an alcohol initiator produces an α-chain end that bears the ester from the initiating alcohol, and hydrolysis of the active tin-alkoxide chain end produces an ω-hydroxyl group amenable towards further transformations.[24] The linear correlation of molecular weights with conversion for both ε-caprolactone and lactide initiated from derivatives of bis-MPA are characteristic of a living polymerization, and importantly, no evidence of adverse transesterification side reactions between either the chains or the ester-based branching junctures is observed.

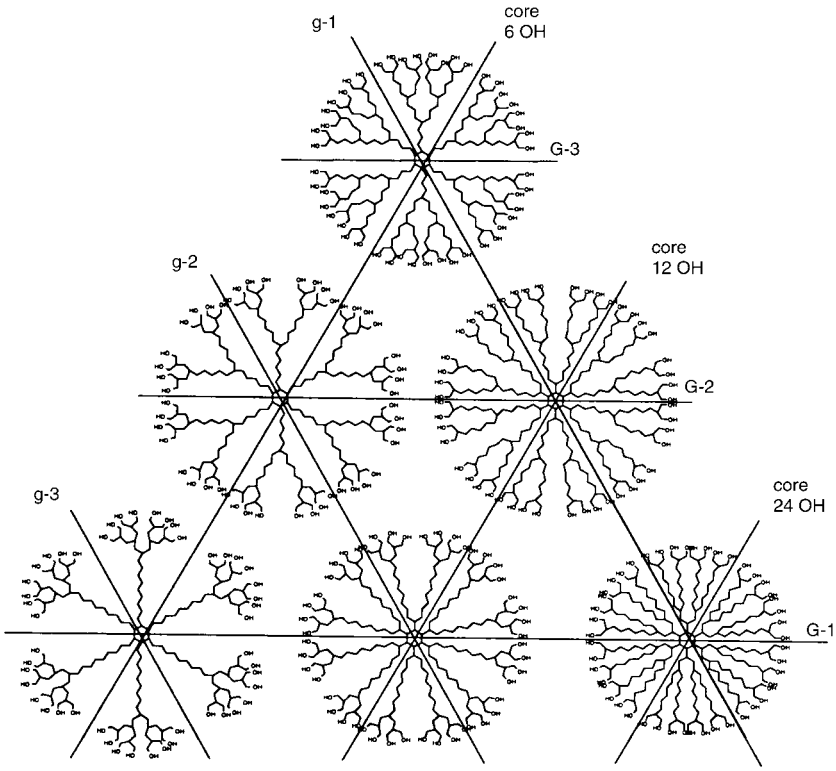
Dendritic polyesters can be prepared as either the dendrimer analogue by a genealogically directed synthesis (divergent growth) comprising of generations of high molecular weight polymer, denoted as dendrimer-like star polymers, or the hyperbranched version generated by the self-polymerization of an AB_x macromonomer. The following paragraphs will describe the synthesis of these macromolecular architectures. Dendrimer-like star polymers were prepared from the combination of living/controlled polymerization procedures and quantitative organic transformations using a divergent growth approach.[25] Two general scaffolds for the construction of dendrimer-like star polymers have been surveyed including the first through third generation dendrimers derived from bis MPA, generating six to twenty-four arms, respectively, and linear poly(caprolactone) containing pendant bis(hydroxymethyl) functionality along the backbone (Scheme 2). Considerable flexibility exists in the construction of the former architecture, as the generation of the dendrimer initiating core, average molecular weight of the polymer, type of polymer and generation of dendron or functionality of the branching juncture between polymer generations can be varied to obtain complex architectures that resemble the most advanced dendrimers. Moreover, the versatility of the synthetic route to dendritic-like star polymers permits variations in the molecular structure between generations,[26] which has enabled materials that, owing to the constraints at the focal points, undergo microphase separation at surprisingly low block molecular weights. Moreover, amphiphilic block copolymers in the form of unimolecular micelles have also been demonstrated.[27]

Small angle neutron scattering (SANS) measurements for the first- and second-generation dendrimer-like star polymers revealed that the radius of gyration scaled with the arm functionality (f) as $f^{2/3}$, in accordance with the Daoud – Cotton model for a multi-arm star polymer.[28] Conversely, the hydrodynamic volumes and radii of gyration of the dendrimer-like star polymers with three generations of poly(ε-caprolactone) were considerably lower than their star or linear analogues. Clearly, the conformation of the dendrimer-like star architecture is considerably more space-filling than a star-shaped macromolecule. In another study, six topological or constitutional isomers of dendrimer-like star polymers



Scheme 2. Examples of dendrimer-like star polymers prepared from different cores: A) linear polycaprolactone core, B) hexafunctional dendritic core.

were prepared each having comparable molecular weights ($\approx$80000 amu mol^{-1}), narrow polydispersities and an identical number of branching points (45) and surface hydroxyl functionalities (48). The general strategy for the design of the topological isomers is best depicted by arranging the dendritic polymers in a triangular schematic (Scheme 3). From the top to the bottom left corner of the triangle, each of the polymers have six-arm star poly(caprolactone) in the central core initiated from the first-generation dendrimer, denoted as the line 6-OH. Likewise, the line denoted as 12-OH represents the polymers initiated from the second-generation dendrimer, whereas line 24-OH denotes the polymer initiated from the third-generation dendrimer. Moving down the triangle from the top to the bottom right corner, these polymers each has the first generation dendron at the polymer surface (line g – 1). Likewise, the lines denoted as g-2 and g-3 are polymers that have the second- or third-generation dendrons at the surface, respectively. The horizontal lines denoted as G-1 through G-3 indicate the number of generations of poly(caprolactone) or the degree of internal branching. The only



Scheme 3. General design strategy for topological isomers of dendrimer-like star polymers.

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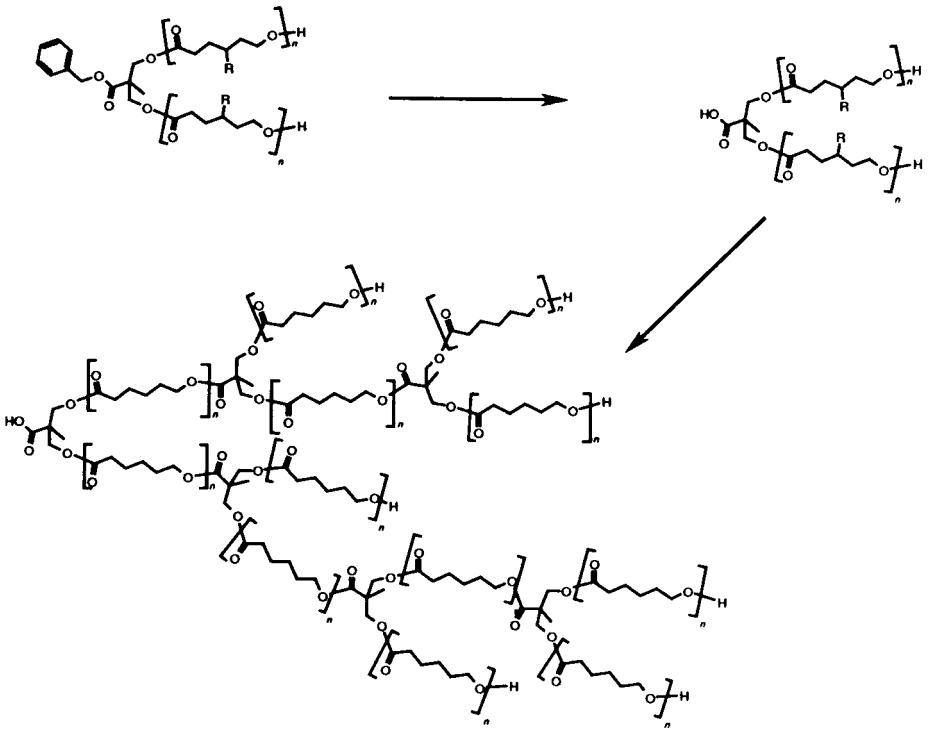
difference in the six isomers is the placement of the branching junctures. SANS measurements yielded values of the R_g which, when combined with hydrodynamic volume measurements obtained by size-exclusion chromatography, confirmed that the radial distribution is consistent with the designed architectures. The most pronounced effects on the physical properties, morphology (crystallinity) and hydrodynamic volume were for the polymers in which the branching was distributed evenly throughout the sample in a dendrimer-like fashion. Hawker et al. reported a similar study on polymer architecture by contrasting the isomers of a dendrimer and its linear analogue.[29]



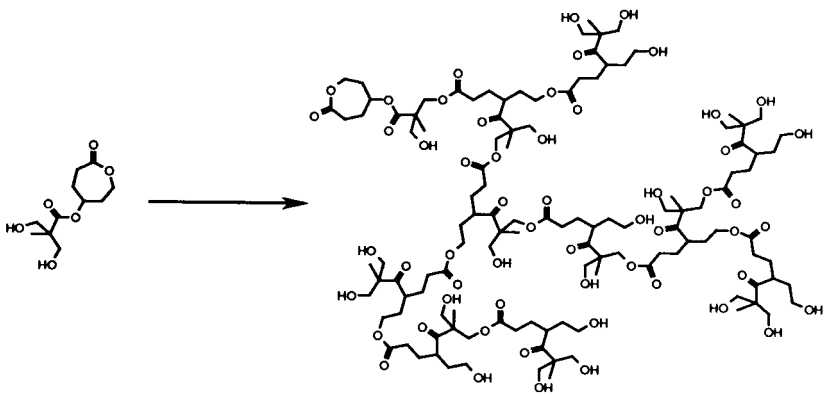
Scheme 4. Hyperbranched polyesters prepared from AB_x macromonomers.

Dendritic polyesters, prepared from AB_x macromonomers,[30] generated the hyperbranched equivalent of a "comb-burst" architecture or the dendrigraft polyesters reported by Jerome in a single-step polymerization (Scheme 4).[16] The macromonomers, initiated from either the first (AB_2) or second (AB_4) generation dendrons of bis MPA, protected as the benzyl ester, generated narrowly dispersed products with molecular weights (4000 to 18000 g mol^{-1}) that closely tracked the monomer to initiator ratio.[30] The benzyl groups on the initiator were removed by catalytic hydrogenolysis, generating the requisite acid functionality and the α-carboxylic,ω-dihydroxy AB_2 macromonomer. Polymerization of the AB_x macromonomer was accomplished using dicyclohexyl carbodiimide (DCC) and 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS) in methylene chloride.[31] High molecular weight hyperbranched polymers were obtained with the expected broadening in polydispersity associated with the condensation polymerization. ^{1}H NMR analysis of the hyperbranched polymers showed a branching pattern which is similar to those polymers prepared by a tedious step-wise divergent approach. Hyperbranched copolymers were prepared by the co-condensation of different AB_x macromonomers. Substituted or functionalized cyclic esters provide a means to modify the dendritic polyester producing properties ranging from thermoplastic elastomers, to rubber toughened systems or amphipilic copolymers.

Alternatively, hyperbranched polyesters have been prepared from self-condensing cyclic ester polymerization using $A(B^*)_x$ monomers (Scheme 5). This one-step approach to hyperbranched polymers was first introduced by Fréchet and later developed by Matyjaszewski, Hawker, Hedrick, and Muller.[32] Cyclic lactones containing either hydroxyl or bis(hydroxymethyl) initiating groups were self-polymerized either with or without additional nonfunctional monomer in the presence of $Sn(Oct)_2$.[33] High molecular weight polymer was obtained with the expected broad polydispersities and the degree of branching was approximately 0.5.

Dendritic-Linear A_xB_y Block Copolymer

Various dendritic-linear A_xB_y block copolymers have been prepared, where the A-blocks are hydrophilic dendrimers derived from bis MPA derivatives and the B-blocks are linear chains of poly(ε-caprolactone) (Scheme 6).[34, 35] The design of these copolymers is versatile, allowing the molecular weight,



Scheme 5. Preparation of hyperbranched polyesters from from a self-condensing $A(B^*)_x$ monomer.

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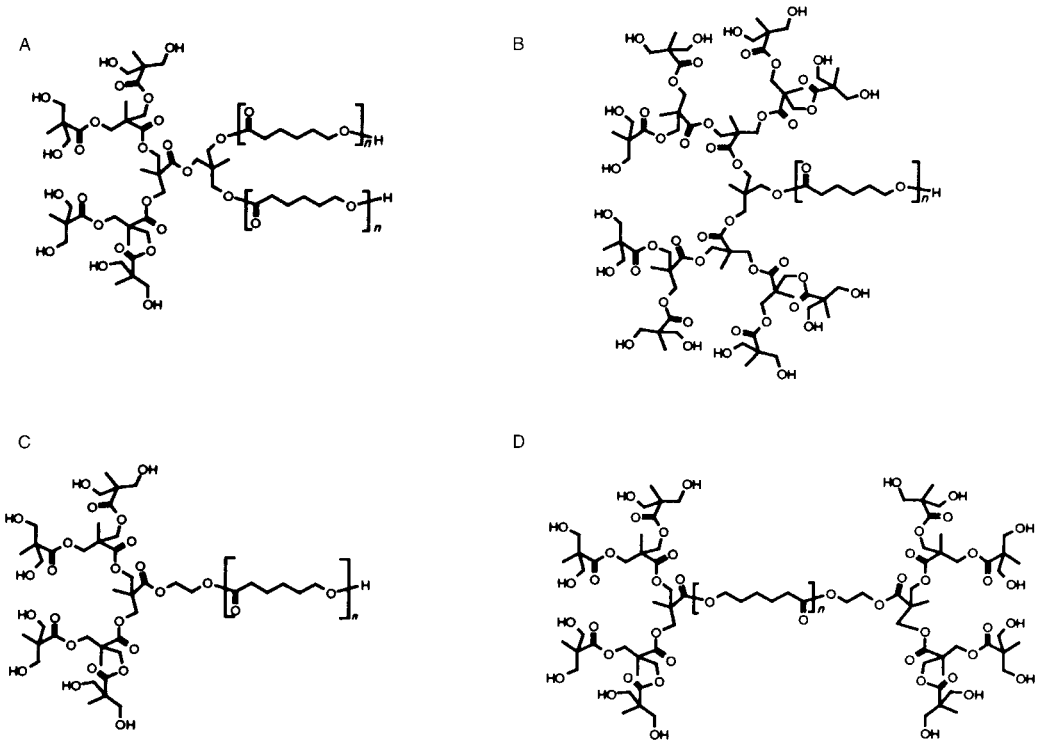
composition and number of poly(ε-caprolactone) blocks or tails to be varied together with the generation and number of dendrons. The versatility in the design stems from the synthesis of various libraries of building blocks employed in the construction of the copolymers including different generations of hydrophilic functional dendrons and novel orthogonally protected multifunctional initiators. Although the use of orthogonal protecting groups is common in organic synthesis, it has been rarely employed as a tool in polymer synthesis. Because of the sensitivity of the poly(ε-caprolactone) and dendrons towards hydrolysis they require mild conditions, protection and deprotection schemes for the initiators as well as the dendrons were judiciously designed. Libraries of new initiators composed of the first through third-generation protected dendrons and hydroxyl groups protected with either benzyl ether or benzylidene acetal groups were prepared. Deprotection of these hydroxyl groups by catalytic hydrogenolysis yielded the requisite nucleophilic initiators for the controlled ROP of ε-caprolactone in the presence of a suitable organometallic promoter. These initiators provided a variety of A_xB_y macromolecular topologies (Scheme 6). Narrowly dispersed products with predictable molecular weights were obtained. NMR and GPC studies of the block copolymers confirmed the efficiency of the orthogonally protected multifunctional initiator approach to dendritic-linear copolymers. Upon deprotection of the surface hydroxyl groups on the dendrons, the macromolecules became amphiphilic, with a polar, hydrophilic head (dendrons) and a nonpolar, hydrophobic tail (linear poly(caprolactone)). These new amphiphiles resemble, in many ways, low molar mass surfactants such as phospholipids, yet retain many of the characteristics of block copolymers. Considerable work on nanostructured materials with unusual properties has been reported using linear polymers with dendritic wedges either decorating the backbone decorated or coupled at the chain-end(s) in an AB or ABA configuration. Appropriately designed dendritic linear hybrid block copolymers are amphiphilic and shape-responsive in properly chosen solvents, forming either monomolecular or supramolecular micelles.[36] In another example, Percec et al. have designed and synthesized spherical and cylindrical supramolecular structures from monodendrons that self-assemble.[37]

Star-Shaped Polyesters through Dendritic Initiation

Another means of mediating dendritic chain-end functionality and molecule size and shape is through polymerization. Star-shaped polyesters were prepared by the controlled polymerization of ε-caprolactone or lactide initiated from the numerous chain-end hydroxymethyl groups of the analogous dendrimeric and hyperbranched polyesters derived from 2,2′-bis(hydroxymethyl) propionic acid (Scheme 7).[38, 39] The initiators chosen for study were generations 2 – 5 of the hydroxy-terminated hyperbranched polyesters reported by Hult and commercially available from Perstorp and the corresponding dendrimers generations 1 – 4. The number average molecular weight per arm correlated closely to the monomer to initiator ratio. By varying this ratio or the size of the initiator, molecular weights ranging from 20000 to 210000 g mol^{-1} could be obtained for the hyperbranched initiators. In a similar fashion, the initiation of ε-caprolactone from the dendrimeric analogues proved to be extremely facile, and gave star polymers with accurate control of molecular weight and narrow polydispersities irrespective of the generation employed. For example, polymerization of



Scheme 6. Representative examples of hybrid dendritic-linear A_xB_y block copolymers.

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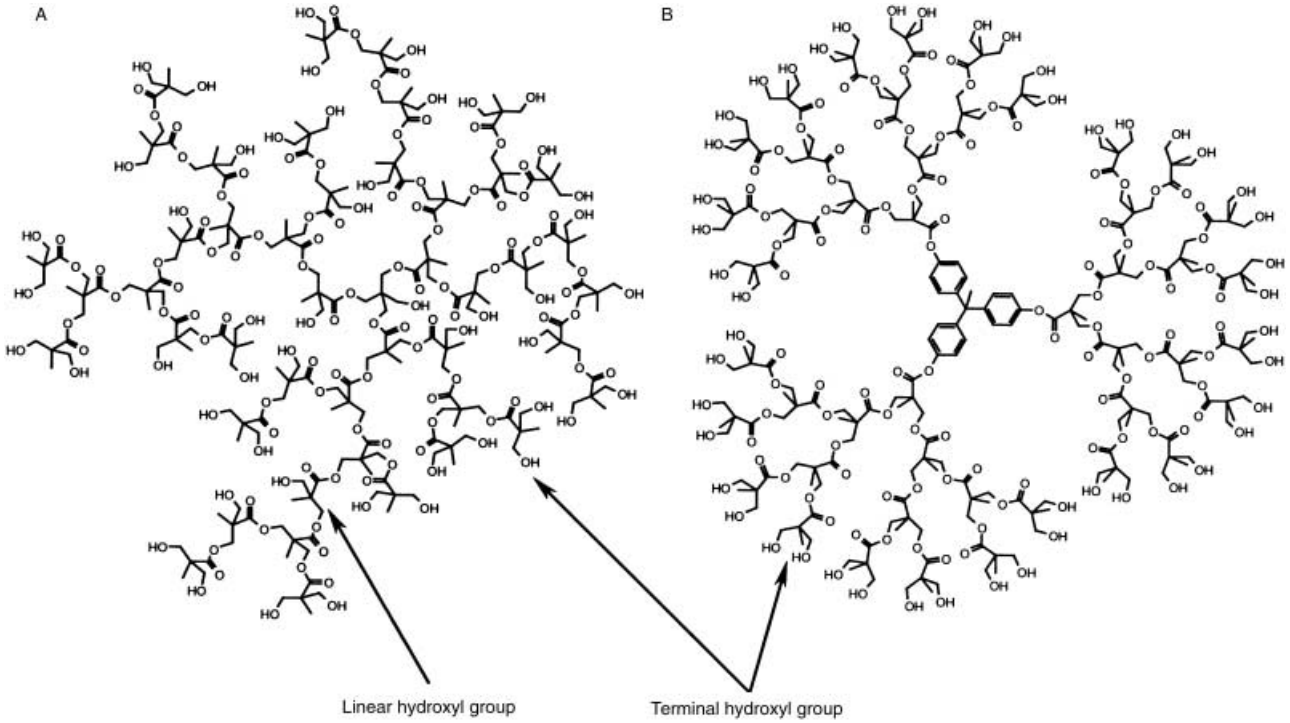


Scheme 7. Structure of dendritic initiators for the synthesis of multi-armed star-shaped polymers; A) hyperbranched core and B) dendrimer-based core.

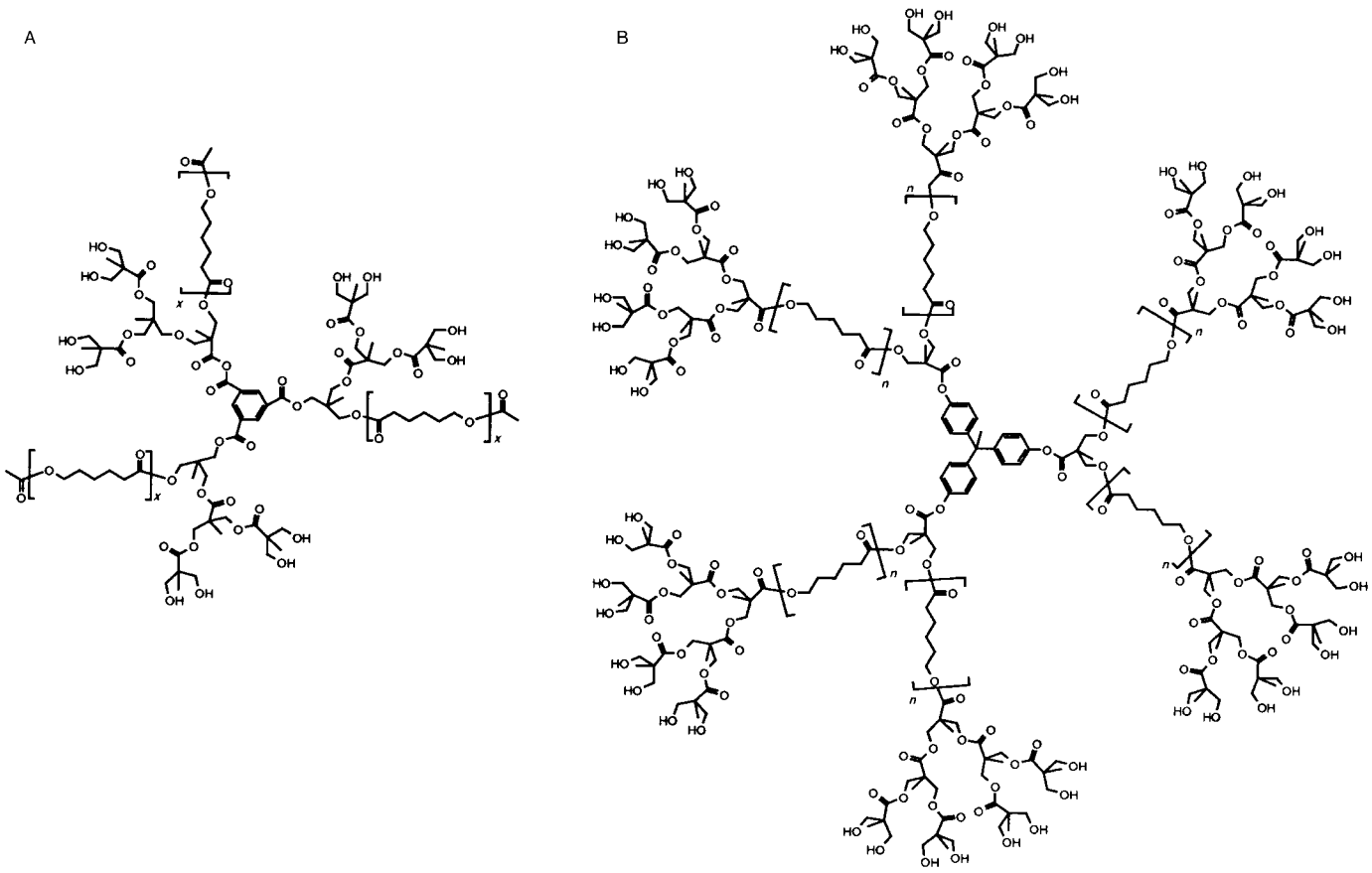
960 molar equivalents of ε-caprolactone with the fourth-generation (G-4) dendrimer (48 surface hydroxyl groups) gave a star-shaped polymer in 96% yield at 110 °C (20 h) ($M_n = 115\,000$ g mol^{-1}, PDI = 1.18). Clearly, the level of polymerization control from the hyperbranched isomer (degree of branching of $\approx$50%) was not as high as achieved with the dendritic analogue (degree of branching 100%) and the difference was correlated to the degree of branching. The reactivity of terminal hydroxyl groups were shown to be higher than the corresponding linear hydroxyl groups, possibly due to a combination of steric and electronic effects. This data is consistent with previous reports on transformations on isomeric hyperbranched, linear and dendrimeric aromatic polyesters.[40]

Dendronized Star Polymers

The modification of star-shaped polymers with functional dendrons provided unique materials with abundant functionality and solution properties somewhat similar to dendritic materials, yet with mechanical properties comparable to the linear analogues. Two general strategies were investigated where dendrons were selectively placed either in the core of the stars (denoted as a miktoarm dendritic-linear star polymers) or decorated at the periphery of the star chain-ends (Scheme 8). The dendritic-linear miktoarm star polymers were prepared using a tandem "core-in"/"core-out" approach utilizing consecutive convergent dendron attachment and ROP.[34] The rational design of orthogonally protected, multifunctional compounds containing sites for the attachment of dendrons in a convergent approach together with an initiator for ROP enabled the synthesis. ^{1}H NMR and SEC measurements of the block copolymers confirmed that the targeted structures were achieved with low polydispersities and predictable molecular weights. Moreover, the nature and size of the arms and dendrons had a significant influence on the hydrodynamic radii and the ability to form self-assembled structures in solution. In the second approach, Mitsunobu[41] conditions were used to couple the hydroxyl-functional star poly(caprolactones) to the focal point of protected dendrons (g-1 – g-2) to produce star polymers with 12, 24, or 48 functional groups upon deprotection.[25] Interestingly, the hydrodynamic volume for the sample functionalized with the third generation dendron was clearly larger than the others and the extended conformation presumably stems from steric crowding associated with the large dendron on the relatively short poly(caprolactone) chains.

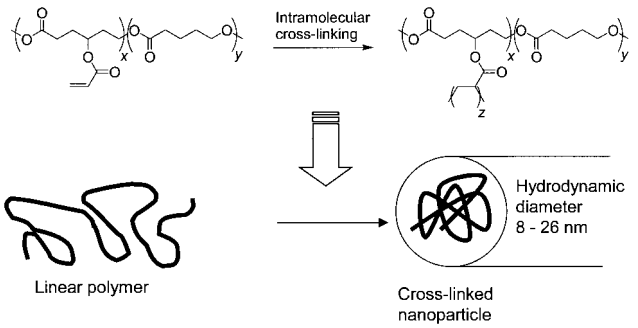
Organic Nanoparticle Formation

An alternative approach to organic nanoparticle formation has provided unique and versatile opportunities to shape-persistent macromolecules that have dimensions characteristic of dendritic polymers.[13d] This approach relies on the controlled intramolecular crosslinking of a functionalized polymer chain. The versatility of shape control is provided by the possible variables, which include the latent crosslink chemistry/density and polymer type, functionality and architecture including, for example, dendronized linear polymers, block copolymers and star-shaped polymers.[42] In one example, linear aliphatic polyesters containing pendant acrylate functionalities[13d, 43] were predominantly self-crosslinked by a radical mechanism in ultradilute conditions generating primarily single chain nanoparticles with only minor amounts of



Scheme 8. Dendronized star polymers; A) miktoarm dendritic-linear star polymer (core functional), B) dendritic-functionality located at the periphery of the arms of the star polymers.

intermolecular coupling (Scheme 9). Hydrodynamic radii varying from 3.8 to 13.1 nm were measured by dynamic light scattering. The size of the particle increased with the molecular weight of the linear precursor polymer for a constant level of crosslinking functionality.



Scheme 9. Basic strategy for the synthesis of single molecule nanoparticles by ultra-high dilution methods.

Porous Organosilicates: The Role of Porogen Architecture

Two general strategies were investigated to generate nanocomposites from silsesquioxanes (SSQ) using the range of three-dimensional polyesters described above; the first involves formation of a simple polymer mixture designed to be miscible initially which undergoes an arrested nucleation and phase separation growth upon SSQ cure, while the second approach relied on a preformed template or nanoparticle to define the hybrid morphology and ultimately the porous structure.[10c, 13d, 15] Mixtures of the SSQ component and various porogens were co-deposited from solution onto silicon wafers by spinning and subsequent baking. The curing of the SSQ component has been extensively studied using a variety of spectroscopic and thermomechanical techniques. The onset of network formation begins at 150 °C and by 250 °C essentially all of the SiOH functional groups are consumed affording an organosilicate with a T_g and related properties comparable to that of a fully cured material. At these temperatures, the polyester is thermally stable. Dynamic mechanical, dielectric and thermal analysis measurements were used to study the morphology of the hybrids, and many of the isomeric porogen architectures investigated were miscible with the SSQ derivatives at low temperatures, provided their molecular weights were low. For each of the hybrids surveyed, a phase-separated morphology was generated during the initial cure (250 °C), but the size scale of phase separation was strongly dependent on the porogen architecture. For example, FESEM micrographs of three representative architectures including linear ($k = 2.0$, pore size > 100 nm), star-shaped ($k = 1.95$, pore size ≈ 30 nm (SAXS)) and hyperbranched ($k = 2.0$, pore size ≈ 18 nm (SAXS)) poly(caprolactone) are shown in Figure 2. The dramatic differences observed for the isomeric porogens is believed

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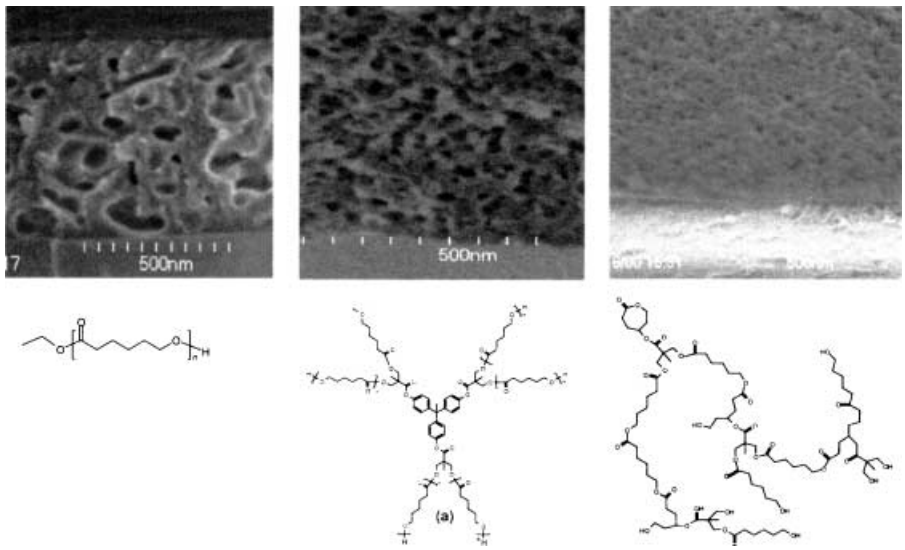


Figure 2. Role of macromolecular porogen architecture on pore size and shape.

to result from the enhanced solubility of the branched materials, facilitated, in part, by the abundant functional chain ends and the chain topology. The improved solubility is believed to postpone phase separation until the later stages of the cure, minimizing coarsening of the morphology. Thermolysis of the macromolecular template generated nanoporous organosilicate films with dielectric constants that tracked the volume fraction of the template.[15]

The second approach to nanoporous organosilicates is based on a predefined polyester template in the form of an organic nanoparticle and is based on the concept that each particle will create a single pore, the size and shape of which are identical to the sacrificial template.[13d] In this way, the initial miscibility of the porogen (particles) with the SSQ is not critical and the phase-separation does not rely on nucleation and growth processes. Instead, the particles need to be homogeneously dispersed in the matrix and then simply "go alone for the ride". Solutions of SSQ and the polycaprolactone nanoparticles were deposited and cured to 430 °C to effect network formation and the decomposition of the nanoparticle. Figure 3 shows the FESEM of the porous SSQ and pores smaller than 10 nm are uniformly distributed throughout the film. The average pore size of the porous organosilicate calculated from small angle X-ray scattering measurements was 7.2 nm, which compares favorably with the size of the crosslinked nanoparticles ($R_h = 6.5$ nm, by dynamic light scattering). The dielectric constant of a porous SSQ prepared from 20 wt.% nanoparticles was 2.1, a considerable reduction from the dense film (2.8).

Summary/Outlook

A modular approach to the design and synthesis of a variety of novel macromolecular architectures including dendritic polymers, star-shaped polymers, dendritic-linear hybrids, dendronized polymers and single chain organic nanoparticles was described. Libraries of dendrimers, dendrons, orthogonally protected multifunctional initiators and living polymerization methods were the key synthetic tools used to create/construct these unique macromolecules. A distinguishing feature of this work is the use of well-defined living polymerization procedures designed to produce generations of high polymer between precisely defined branching junctures. Molecular weights up to 250000 g mol^{-1} are readily obtained after just three generations, and purification between transformation steps is generally accomplished by a simple polymer precipitation. With this strategy, these topologically unique materials may be tailored in ways typical of their linear analogues including block and random copolymerization, the generation of either semi-crystalline or amorphous morphologies, amphiphiles etc. The distinctive attributes of these macromolecules, designed to enhance solubility through amplified end-group functionality, were exploited to minimize phase separation in simple mixtures with organosilicates. Current work focuses on new synthetic strategies for the ROP of cyclic esters and ethers. Since many of these metal-containing catalysts for the ROP of lactide and lactone remain bound to the chain-ends, removal of this contaminant is mandatory and costly for microelectronic applications. Recently, a metal-free organocatalytic approach to ROP using tertiary amines, phosphines and N-heterocyclic carbenes as nucleophilic catalysts has been developed as a route to well-defined macromolecules (see Scheme 10).[44] These develop-

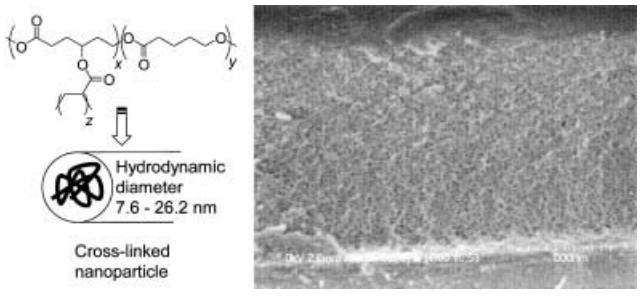
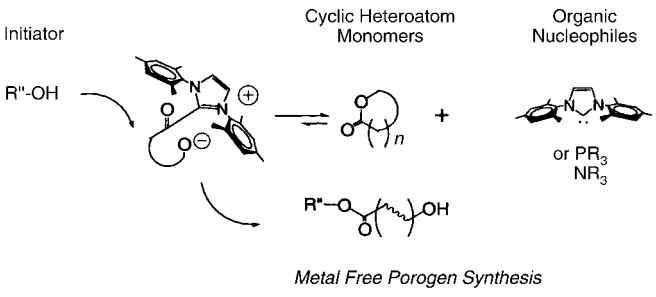


Figure 3. FESEM micrograph of nanoporous organosilicate from nanoparticle template.



Scheme 10. General strategy for the organocatalytic ring opening polymerization of cyclic lactones.

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ments will be incorporated to the library of building blocks for the construction of new macromolecular architectures.

Two general strategies were described to nanocomposites of SSQ using the various isomeric versions of polyesters; the first involved simple polymer mixtures designed to initially be miscible which then undergo an arrested nucleation and growth phase separation upon cure, while the second approach relied on a preformed template in the form of an organic nanoparticle to establish the hybrid morphology and ultimately the porous structure. The different isomeric versions of the porogens were shown to have a pronounced effect on the size scale of phase-separation in the hybrids and ultimately the properties of the nanoporous materials.

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