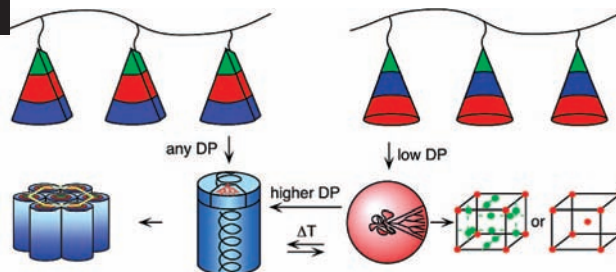# Induced Helical Backbone Conformations of Self-Organizable Dendronized Polymers

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CONSPECTUS

Control of function through the primary structure of a molecule presents a significant challenge with valuable rewards for nanoscience. Dendritic building blocks encoded with information that defines their three-dimensional shape (e.g., flat-tapered or conical) and how they associate with each other are referred to as self-assembling dendrons. Self-organizable dendronized polymers possess a flat-tapered or conical self-assembling dendritic side chain on each repeat unit of a linear polymer backbone. When appended to a covalent polymer, the self-assembling dendrons direct a folding process (i.e., intramolecular self-assembly). Alternatively, intermolecular self-assembly of dendrons mediated by noncovalent interactions between apex groups can generate a supramolecular polymer backbone.

Self-organization, as we refer to it, is the spontaneous formation of periodic and quasiperiodic arrays from supramolecular elements. Covalent and supramolecular polymers jacketed with self-assembling dendrons self-organize. The arrays are most often comprised of cylindrical or spherical objects. The shape of the object is determined by the primary structure of the dendronized polymer: the structure of the self-assembling dendron and the length of the polymer backbone. It is therefore possible to predictably generate building blocks for single-molecule nanotechnologies or arrays of supramolecules for bottom-up self-assembly.

We exploit the self-organization of polymers jacketed with self-assembling dendrons to elucidate how primary structure determines the adopted conformation and fold (i.e., secondary and tertiary structure), how the supramolecules associate (i.e., quaternary structure), and their resulting functions. A combination of experimental techniques is employed to interrogate the primary, secondary, tertiary, and quaternary structure of the self-organizable dendronized polymers. We refer to the process by which we interpolate between the various levels of structural information to rationalize function as retrostructural analysis. Retrostructural analysis validates our hypothesis that the self-assembling dendrons induce a helical backbone conformation in cylindrical self-organizable dendronized polymers. This helical conformation mediates unprecedented functions.

Self-organizable dendronized polymers have emerged as powerful building blocks for nanoscience by virtue of their dimensions and ability to self-organize. Discrete cylindrical and spherical structures with well-defined dimensions can be visualized and manipulated individually. More importantly, they provide a robust framework for elucidating functions available only at the nanoscale. This Account will highlight structures and functions generated from self-organizable dendronized polymers that enable integration of the nanoworld with its macroscopic universe. Emphasis is placed on those structures and functions derived from the induced helical backbone conformation of cylindrical self-organizable dendronized polymers.

Introduction

Dendronized polymers are an archetypal polymer architecture from which we can derive new concepts for single-molecule and bottom-up self-assembly of nanotechnologies.[1,2] These polymers are comprised of a linear polymer backbone with

SCHEME 1. Self-Organizable Dendronized Polymers Concept[a]
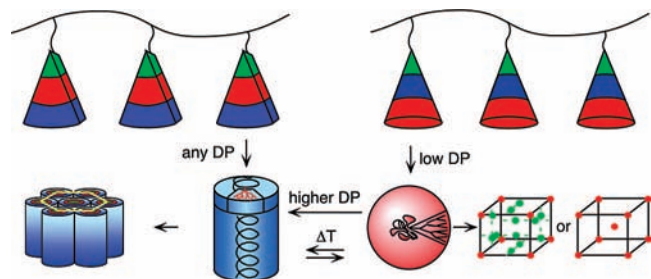
[a] DP = degree of polymerization.

a dendritic side chain attached to each repeat unit (Scheme 1). In a landmark experiment, Tomalia demonstrated that a linear poly(ethyleneimine) could be used as the core for the divergent synthesis of propyleneimine dendron side chains.[3,4] The convergent synthesis of benzyl ether dendrons introduced by Hawker and Fréchet[5] was used for the synthesis of dendronized polymers. In addition to our efforts using first-generation self-assembling dendrons,[6–8] other groups demonstrated that higher generation benzyl ether dendrons could be employed in the synthesis of dendronized polymers.[9,10] Unlike Fréchet-type benzyl ether dendrons, which are amorphous,[5] self-assembling dendrons have an amphiphilic structure that allows them to form ordered arrays.[11,12]

Dendronized polymers containing self-assembling dendrons form cylindrical or spherical objects whose diameters are defined on the nanoscale ($\sim$30–100 Å). The fully extended length of the cylindrical dendronized polymers can be many orders of magnitude larger. Discrete cylindrical and spherical structures with well-defined dimensions were visualized and manipulated individually.[13] Such features are desirable for top-down assembly of nanostructures and devices. Importantly for bottom-up self-assembly, the self-assembling dendrons allow the resulting cylindrical or spherical dendronized polymers to spontaneously generate periodic or quasiperiodic arrays.[13] We refer to this process as self-organization and to the supramolecules as self-organizable dendronized polymers. Since the outset, we have been concerned with the internal structure of the cylindrical self-organizable dendronized polymers. The aim of this Account is to survey the potential of self-organizable dendronized polymers to bridge the integration gap between nano-, micro-, and macroscopic structures and functions.

Bio-Inspired Design of Self-Organizable Dendronized Polymers

The strategies to generate cylindrical and spherical dendronized polymers with covalent or supramolecular backbones were inspired by the self-assembly of tobacco mosaic virus

(TMV) and of icosahedral viruses.[14,15] TMV contains 2130 identical protein subunits that self-assemble in the presence of viral RNA[16] (Scheme 2a,b) and in its absence[17] (Scheme 2c). When combined with the viral RNA, the protein subunits define the shape of the helical assembly while the RNA adopts a helical conformation and defines the length of the rod-like helical virus. Viral assembly is nucleated by insertion of a hairpin RNA into the central hole of the protein disk and in between the two layers of subunits. In the absence of the RNA component the protein subunits self-assemble into discs that further organize into helical structures.

Scheme 3 illustrates our general approach to preparing cylindrical and spherical polymers containing covalent and supramolecular backbones. These polymers are based on amphiphilic self-assembling dendrons, which play a role similar to the protein subunits of TMV. Each tier in Scheme 3 identifies a unique level of structural correlation from primary structure that involves the chemical composition and its sequence (not shown) at the molecular level through to two- and three-dimensional order in the supramolecular structure and its self-organized lattice. Across the top row are geometric shapes that describe the conformations of the self-assembling dendrons. The bottom row of Scheme 3 illustrates the lattice symmetries of the various self-organized dendronized polymer arrays. This Account will focus mostly on dendronized polymers self-organized in columnar and cubic lattices. The cubic bicontinuous lattice (*Ia*$\bar{3}$*d*) was discussed elsewhere.[18] The middle row illustrates the molecular self-assemblies that comprise each lattice; these are individual dendronized polymers.

Elucidation of any one tier requires structural analysis using a combination of characterization techniques[11,19] that will not be discussed here, while the interrelationships that mediate increasingly complex hierarchical order build upon information from each stage. We refer to the process of interpolating between information gleaned from each individual tier as retrostructural analysis.[11,12] Retrostructural analysis is made possible by self-organization that arises from jacketing polymer backbones with self-assembling dendrons.

Self-Organizable Dendronized Polymers with Covalent Backbones

Three different strategies are employed to prepare dendronized polymers with covalent backbones. The attach-to strategy combines preformed linear polymers with self-assembling dendrons. Such an approach was used with first-generation self-assembling dendrons attached via hydrosilation to poly(methylsiloxane)s.[6] A second approach involves polym-

SCHEME 2. (a) The Self-Assembly Reaction of Tobacco Mosaic Virus (TMV)[a], (b) Nucleation of the Virus Assembly via the Insertion of a Hairpin RNA into the Central Hole of the Protein Disc, Which Transforms into a Lock-Washer Arrangement[b] and (c) Phase Diagram of the Self-Assembly of TMV A-Proteins in the Absence of Viral RNA[c]
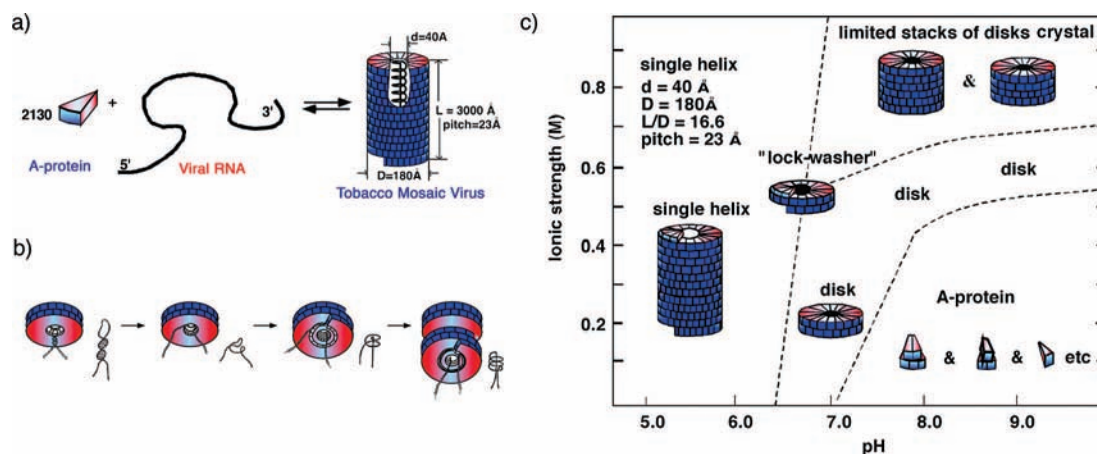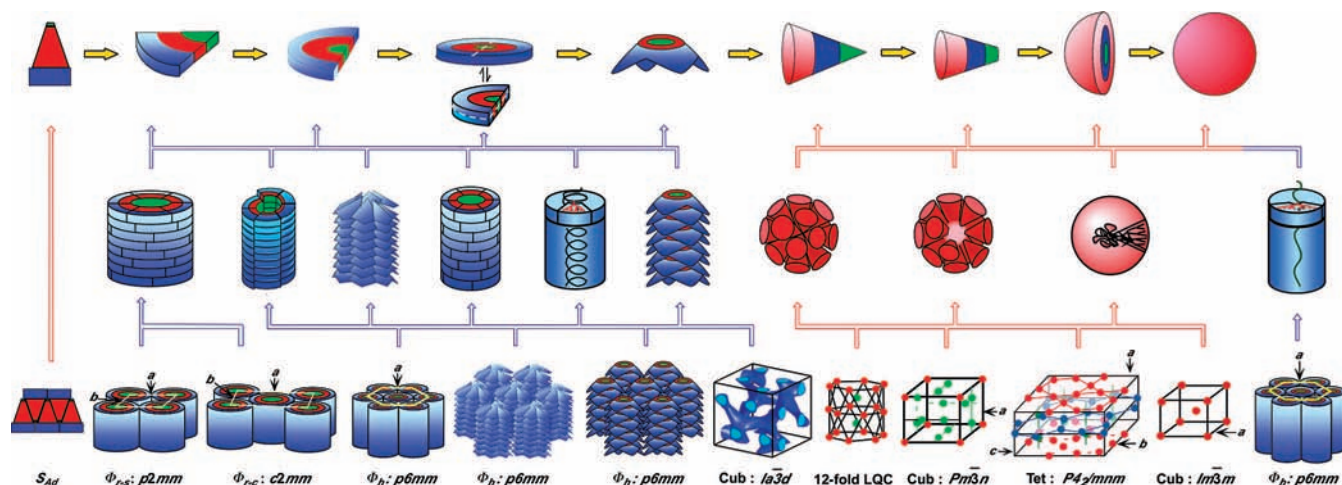

[a] Adapted with permission from ref 15. Copyright 1991 Elsevier.
[b] Adapted with permission from ref 14. Copyright 1983 Wiley-VCH.
[c] Adapted from ref 17. Copyright 1971 Nature Publishing Group.

SCHEME 3. Structural and Retrostructural Analysis of Dendronized Polymers Containing Covalent or Supramolecular Backbones[a]

[a] Reproduced with permission from ref 12. Copyright 2007 American Chemical Society.

erization of dendritic monomers, which was demonstrated by conventional radical[7] and living cationic[8] polymerization of first-generation dendritic methacrylate and vinyl ether monomers, respectively. Most recently, a supramolecular attach-to strategy was introduced.[18] Noncovalent association of electron-donor or -acceptor polymers with semifluorinated dendrons containing complimentary acceptor or donor groups at their apex formed dendronized polymers.[20]

Self-Organizable Dendronized Polymers with Supramolecular Backbones

Supramolecular polymer backbones are generated by self-assembly of the dendrons mediated by interactions between apex groups. We originally introduced a strategy to prepare polymers with a supramolecular backbone via complexation

of alkali metal salts by crown ethers.[21–23] This was further extended to oligo(ethylene oxide) apex groups.[24] Hydrogen bonding between self-assembling dendritic dipeptides generates a helical noncovalent polymer backbone (Scheme 4).[25–32]

Self-organizable dendronized polymers containing self-assembling twin dendrons,[33,34] tapered dendrons attached to the backbone from their periphery rather than their apex,[35] and willow-like dendrons[36] also distort the random-coil conformation of their backbone. They are not reviewed here.

Control of Polymer Shape and Backbone Conformation

The shape of the polymer depends on the degree of polymerization of the backbone, the composition of the self-assembling dendron, and the connection between the dendron and

(4-3,4,-3,5)12G2-CH₂-Boc-ʟ-Tyr-ʟ-Ala-OMe
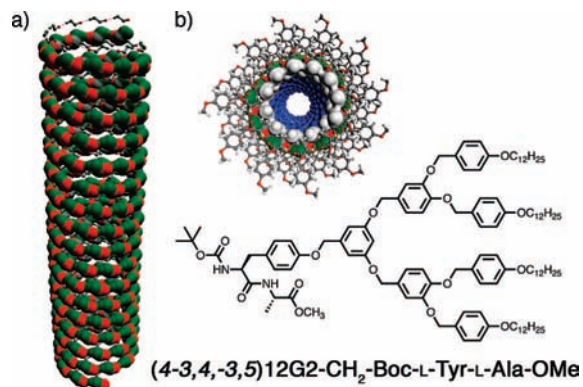
ᵃ Reproduced with permission from ref 27. Copyright 2005 Wiley-VCH.

the backbone. Disc-like structures formed by polymers of extremely low degree of polymerization (DP ≈ 4−5) jacketed with flat-taper self-assembling dendrons stack into cylindrical assemblies that self-organize into columnar lattices.[8,37,38] Cylindrical polymers that self-organize into columnar lattices are obtained at higher DP.[13,38,39] At low DPs, polymers jacketed with conical dendrons exhibit micellar cubic lattices with $Pm\bar{3}n$ and $Im\bar{3}m$ symmetry at low DPs.[13,37−41] When the backbone DP exceeds the maximum number of conical dendrons that can be accommodated in a sphere, the polymer adopts a cylindrical shape. The transformation of a spherical polymer into a cylindrical polymer is due to the quasiequivalence[13] of the dendron conformation, which changes from conical to flat-taper.[13,38,39,42] The polymer shapes identified by X-ray diffraction (XRD) are corroborated by atomic force microscopy (AFM).[13] Shown in Figure 1 are AFM images of individual polymer chains on a graphite surface. The stiffness of the backbone of the dendronized polymers is controlled by the size of the dendron,[13,39] which is determined by the generation and branching pattern of the dendron. Supramolecular backbones rely upon weak interactions that stabilize the preferred shape of the dendron self-assembly. Complexes of dendritic crown ethers with alkali metal salts provide a representative case.[21−23]

Induction of helicity on flexible polymer backbones (e.g., poly(styrene)s and poly(methacrylate)s) arises through restricted conformational freedom due to the steric restrictions of the dendron. A nonhelical and two possible helical arrangements of the dendrons comprising a cylindrical macromolecule emerged based on XRD experiments (Scheme 5). In these models, the dendrons are arranged in a helical pattern tilting toward the column axis. While a helical model for the arrangement of the dendrons about the polymer back-
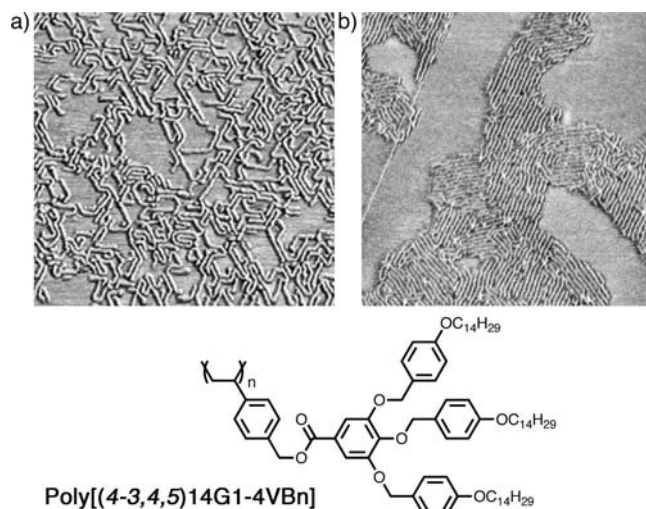

FIGURE 1. Individual cylindrical **poly[(4-3,4,5)14G1-4VBn]** macromolecules visualized by AFM on highly ordered pyrolitic graphite (a) as prepared by spin-casting and (b) after annealing. Reproduced with permission from ref 39. Copyright 1998 American Chemical Society.

bone was preferred, the three models could not yet be discriminated experimentally.[43] Interpretation of light scattering results and conformational analysis of individual macromolecules visualized by AFM for self-organizable dendronized polymers were consistent, depending on the dendron, with a helical conformation or an extended conformation of the backbone.[39,44] Solid-state NMR spectroscopy supports the presence of a helical arrangement of the polymer backbone based on a large mobility gradient: least mobility at the core of the cylinder and most at the periphery (Figure 2).[45] Helical order was also postulated based on XRD and solid-state NMR spectroscopy for self-organizable dendronized polymers prepared by the supramolecular attach-to approach.[20] Although these experimental results indicate only the arrangement of dendrons, a random helical conformation was proposed for a single polymer chain penetrating the cylindrical object.[44] That is, there is no preferred helical handedness, and helix reversals may occur frequently.

Self-Organizable Dendronized Polymers with a Preferred Helical Handedness

Polymers, such as poly(oxanorbornene)s, poly(*N*-arylmaleimide)s, and *cis*-poly(arylacetylene)s, whose backbone structure restricts the available degrees of conformational freedom may induce a helical conformation. Wide-angle XRD of oriented samples of the quality necessary to confirm helical order within the columnar mesophases of self-organizable dendronized poly(oxanorbornene)s and poly(*N*-arylmaleimide)s have not been accessible.[46] Modeling studies to fit the available XRD results led to 3_1- and 7_2-helical models for the back-

SCHEME 5. Lateral and Axial Projections of Possible Models for the Structure of the Supramolecular Cylindrical Columns Formed by **poly[(4-3,4,5)12G1-4EO-MA]**: (a) 8-fold Stacked Disk Structure; (b) 8_1 Helix; (c) 8_4 Helix—The Polymer Backbone Is Not Shown[a]

a   b   c
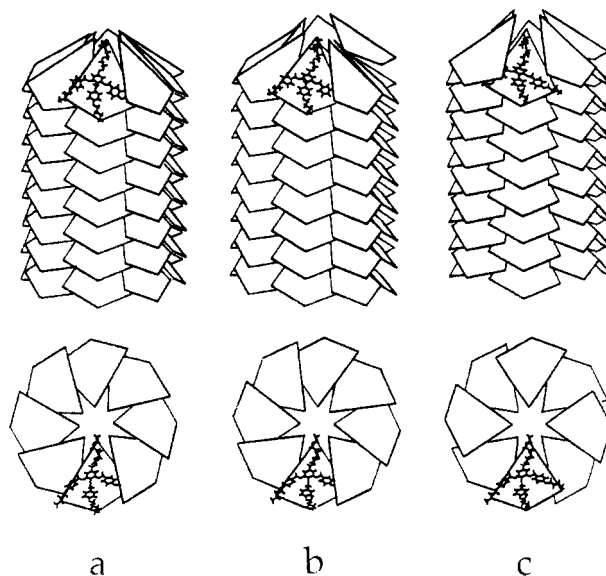
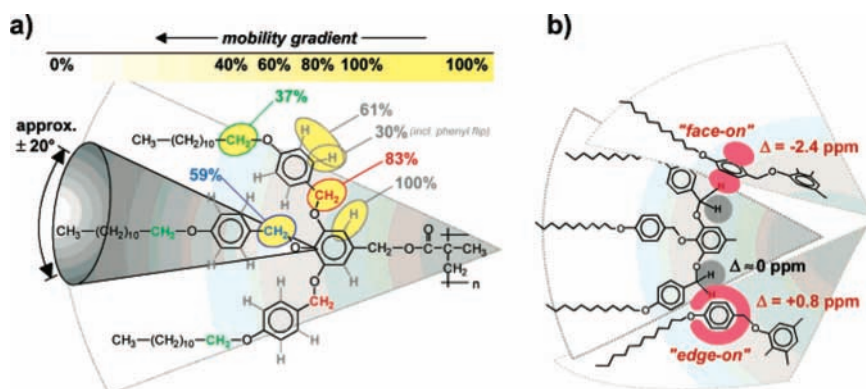[a] Reproduced with permission from ref 43. Copyright 1994 American Chemical Society.

FIGURE 2. Characteristic features of the molecular dynamics and packing of the dendrons in **poly[(4-3,4,5)12G1-MA]**: (a) a mobility gradient along the dendrons is obvious from the local order parameters; (b) "face-on" and "edge-on" types of contacts between dendrons can be derived from the highlighted ^1H chemical shift effects. Reproduced with permission from ref 45. Copyright 2003 American Chemical Society.

bones within a cylindrical self-organizable dendronized poly(oxanorbornene) and a self-organizable dendronized poly(*N*-arylmaleimide), respectively.[46] The UV–vis absorption associated with the conjugated polyene backbone of *cis*-poly(arylacetylene)s provides a handle by which the backbone conformation can be assessed using circular dichroism (CD) spectroscopy.[47] Although the helical conformation is dynamic, the handedness of the helix can be selected by chiral, nonracemic substituents on the aromatic ring.[48]

Self-organizable dendronized *cis*-poly(phenylacetylene)s (*cis*-PPAs),[49–53] poly(1-naphthylacetylene)s,[54] and poly(ethynylcarbazole)s[55] have been shown to adopt a helical conformation in bulk and in solution. XRD of oriented fiber samples of selected examples of these dendronized polymers provides unequivocal evidence for helical order within the columns in

the self-organized lattice (Figure 3).[49–54] CD spectra measured in solvents selective for the peripheral alkyl chains confirm that the polyene backbone handedness can be biased by chiral, nonracemic dendrons (Figure 4).[49–55] Although the dendrons significantly reduce backbone mobility in bulk,[45] we observe dynamic helical behavior in solution.[49–55] Exciton coupling analysis (Figure 5) was employed to assign the handedness of **poly[(4Pr-3,4,5Pr)12G1-EO*-PA]** to a right-handed helix.[52]

Structural parameters for biasing the helical handedness have been elucidated through structural and retrostructural analysis of libraries of dendronized *cis*-PPAs. The mechanism for transfer of chiral information was shown to be via steric communication.[50] Small differences in the helical backbone pitch caused by peripheral chiral information result in a pro-
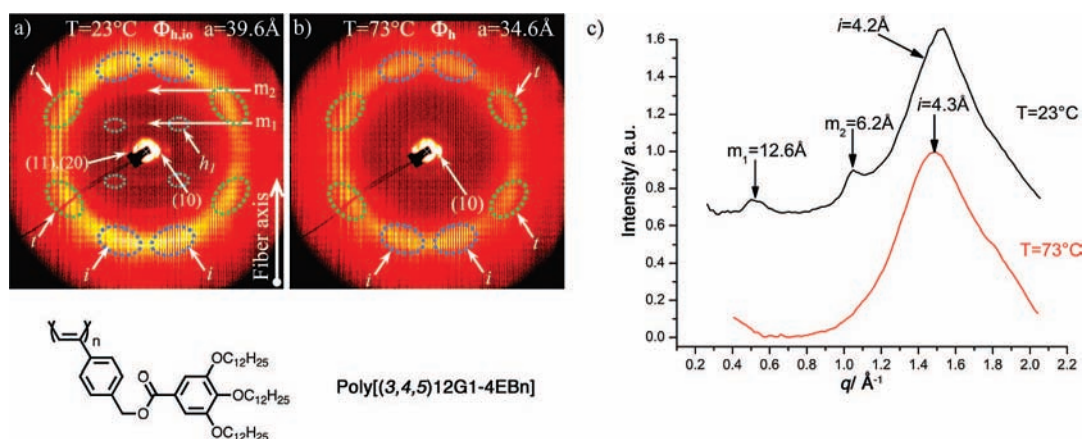
FIGURE 3. (a, b) Wide-angle X-ray diffraction (XRD) patterns from **poly[(3,4,5)12G1-4EBn]** and (c) the corresponding stack meridional plots. Meridional (m_1 and m_2) and long-range (h_1) helical features are highlighted. Adapted with permission from ref 51. Copyright 2006 Wiley-VCH.
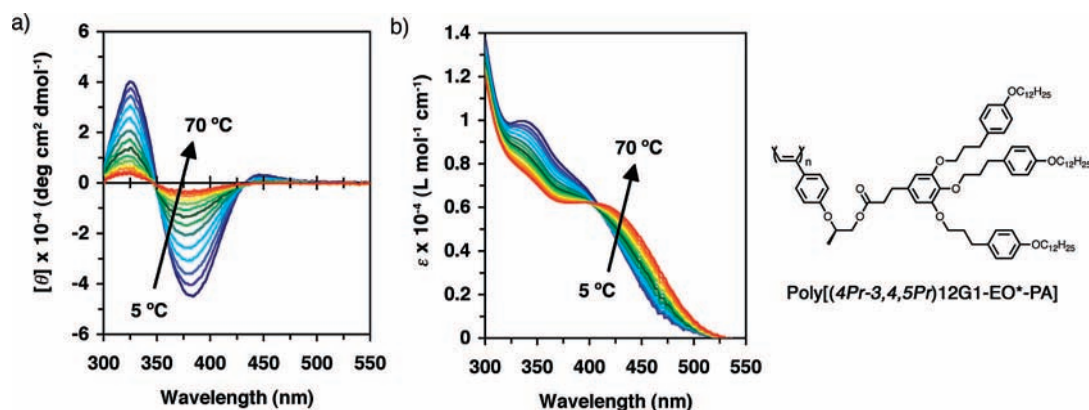

FIGURE 4. Variable-temperature CD (a) and UV–vis (b) spectra from the second heating cycle of **poly[(4Pr-3,4,5Pr)12G1-EO*-PA]** in methylcyclohexane ([rpu] = 8.4×10^{-4} M). Adapted with permission from ref 52. Copyright 2007 Wiley-VCH.
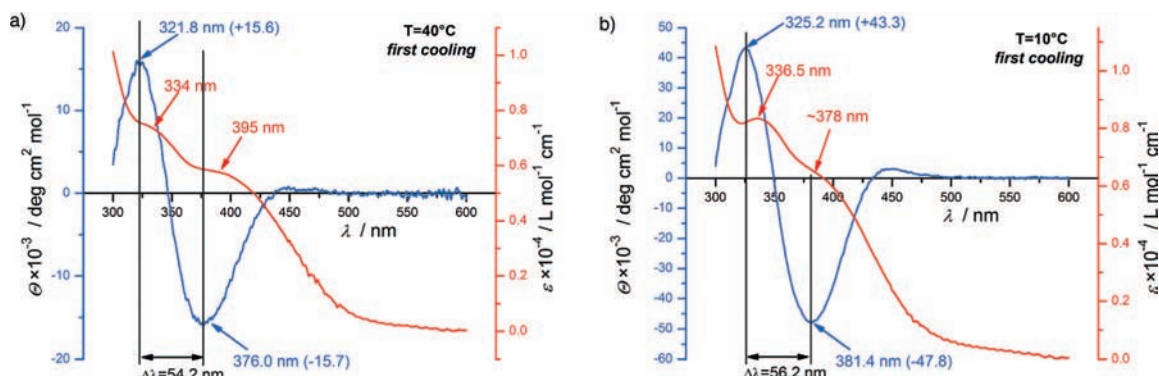

FIGURE 5. Overlays of CD (left axis) and UV–vis (right axis) spectra at (a) 10 and (b) 40 °C from the first cooling of **poly[(4Pr-3,4,5Pr)12G1-EO*-PA]** in methylcyclohexane ([rpu] = 8.4×10^{-4} M). Reproduced with permission from ref 52. Copyright 2007 Wiley-VCH.

nounced increase of the helical handedness. The ability to bias helical handedness from a second generation dendron was made possible by matching the helical pitch of the self-assembling dendron to that of the *cis*-PPA.[49] Closer proximity of the chiral information to the polymer backbone makes biasing the helical handedness easier.[49,50,54,55] Furthermore, polymer backbones that adopt a more compact helical pitch allow for more efficient communication of chiral information from the periphery of the dendronized polymer.[55]

Dendronized polymers containing supramolecular helical backbones present an even greater challenge for selecting a preferred helical handedness. The dynamic nature of the noncovalent backbone might allow for rapid helix inversion, whereas a covalent backbone has fewer degrees of freedom.

Alternatively, the dynamic nature of the noncovalent helical backbone might allow the backbone to more readily anneal into the most stable helical arrangement, whereas this process could be much slower for covalent polymers. Dendritic dipeptides[25] generate a helical supramolecular polymer backbone through hydrogen bonds within the core of the cylindrical assembly. XRD experiments confirm that the helix is present in bulk.[25] CD spectroscopy shows a preferred handedness to the helical arrangement of the dendrons.[25]

A comprehensive library of dendritic dipeptides was subjected to structural and retrostructural analysis in bulk and solution.[25–31] The combined observations have been assimilated into models for the helical assembly, which allow detailed insight to the internal structure. Levers for altering the helical assembly include choice of amino acids at the apex,[25,26] their stereochemistry,[25,27,28] and terminal protecting groups.[29] The structure of the dendron (branching pattern, generation, and peripheral alkyl chain length) plays a critical role for the expression of chiral information at the core of the dendronized polymer and attenuating the hydrogen bonding pattern that constitutes the supramolecular backbone (Scheme 4). These features manifest in a parameter that we refer to as the molecular projected solid angle (α').[25,27–31]

Helical internal order with cylindrical dendronized polymers with covalent and supramolecular backbones is programmable from the primary structure of the constituent dendrons. XRD and CD spectroscopy agree that the dendrons and the backbone are disposed in a helical arrangement, but it remains to be shown by other visualization techniques (e.g., AFM). Comparison of the structural and retrostructural analysis of self-organizable dendronized polymers with helical backbones to those with more flexible backbones shows striking similarity.[51] This validates the helical model postulated earlier for flexible covalent and supramolecular backbones.

Mediating Chemical Reactivity

Appending polymerizable groups with self-assembling dendrons affords a nanoreactor environment wherein an unprecedented self-encapsulated, self-accelerated, and self-controlled polymerization can occur (Scheme 6).[56] Above a critical monomer concentration, self-assembly creates an (effective) increase in the monomer concentration and decreases the initiator efficiency (f) by localizing the polymerizable groups and slowing monomer diffusion. Steric hindrance around the growing chain lowers the rate constant of termination (k_t) such that extremely high molar mass dendronized polymers are obtained in very high conversion and short reaction times using short half-life initiators. For example, polymerization of

SCHEME 6. Evolution of Polymer Shape and Self-Organized Lattice as a Function of Degree of Polymerization[a]
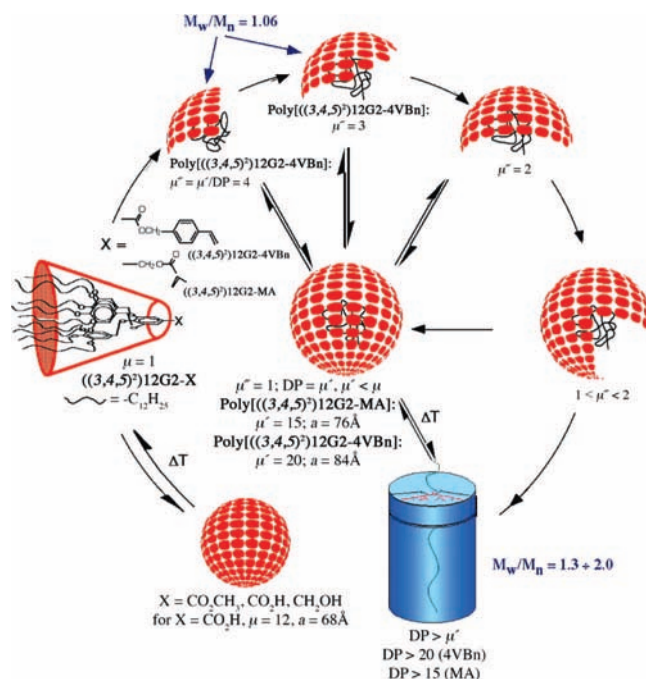
[a] Reproduced with permission from ref 13. Copyright 1998 the Nature Publishing Group.

(3,4,5-3,5)12G2-MA reached 78% conversion in 5 min and yielded a polymer having relative molar mass determined by gel permeation chromatography $M_{n,GPC} = 404\,500$.[39] However, due to its stiff helical conformation, its absolute molar mass is more than ten times larger.[39] In dilute ideal solution, a high number of propagating radicals are generated because monomer diffusion and f increase yet k_t remains low. Using a long half-life initiator minimizes the number of propagating radicals such that nearly monodisperse polymers of low DP are obtained in a controlled, living-like polymerization. This lead us to postulate that self-interruption of a living polymerization in dilute ideal solution would yield monodisperse polymers. Living ring-opening metathesis polymerization of a conical dendritic monomer appears to only form low DP spherical polymers regardless of available monomer but suffers from side reactions that cleave the polymer backbone.[57] Thus a truly self-interrupted polymerization remains to be accomplished.

Self-organizable dendronized *cis*-PPAs prevent thermally induced electrocyclization of the polyene backbone.[49] *cis*-PPAs undergo thermally induced 6π-electrocyclization and oxidative cleavage along the polyene backbone (Scheme 7).[58,59] An unprecedented thermoreversible cisoid-to-transoid conformational isomerization of the *cis*-PPA backbone with increasing temperature suggests a mechanism by which the dendrons prevent 6π-electrocyclization.[49] Figure 6 illustrates features identified by retrostructural analysis of the internally ordered

SCHEME 7. Structural Transformations of the Polyene Backbone in *cis*-PPAs[a]
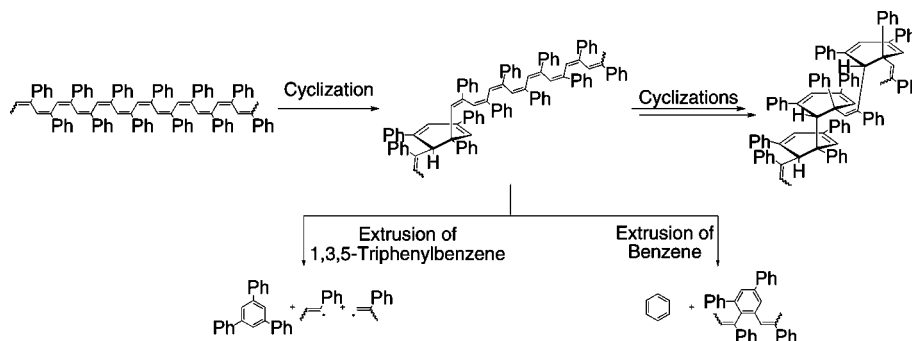
[a] Reproduced with permission from ref 58. Copyright 2005 American Chemical Society.
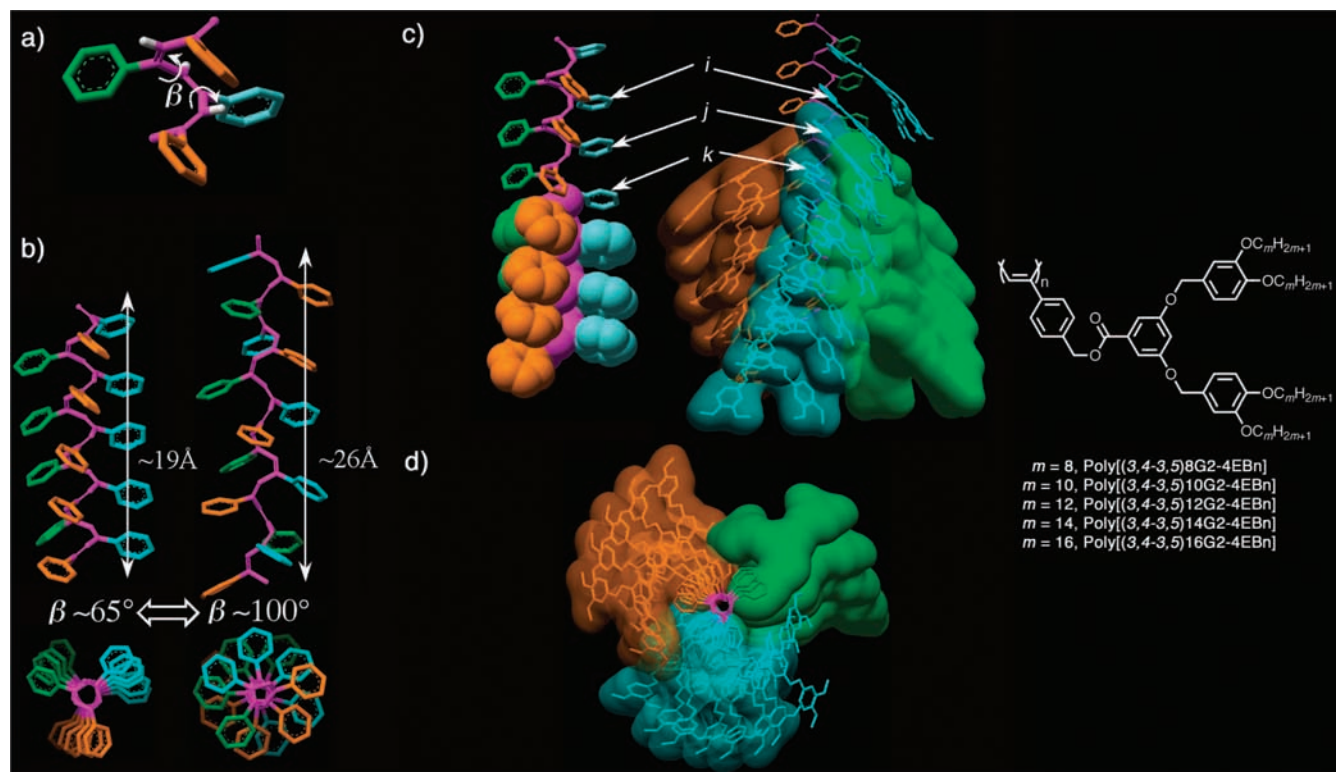

FIGURE 6. Models illustrating the thermoreversible cisoid-to-transoid conformational isomerism and porous columnar structure of **poly[(3,4,-3,5)*m*G2-4EBn]**. Adapted with permission from ref 49. Copyright 2005 American Chemical Society.

hexagonal columnar (Φ_h^{io}) and hexagonal columnar (Φ_h) lattices corresponding to the cisoid and transoid conformations, respectively.[49] In the conformation, $C(1)$ and $C(6)$ of the 1,3,5-hexatriene sequence along the *cis*-PPA backbone are too far apart to undergo electrocyclization. In the cisoid conformation, the steric bulk of the dendrons impedes or prohibits the bond rotations that occur during electrocyclization.

Charge Transport in Self-Organizable Dendronized Polymers

Enhanced charge transport in supramolecular materials has been demonstrated using self-organizable dendronized polymers. A supramolecular polymer backbone is obtained from self-assem-

bling dendritic crown ethers in the presence of alkali metal salts.[22] The increased ion conductivity through the film in the Φ_h phase is mediated by migration of ions within the ordered supramolecular polymer.[22] Complex electronic materials having a covalent polymer backbone have also been prepared via the supramolecular attach-to strategy.[20] The electron donor–acceptor complex formed between the self-assembling dendrons and electroactive polymer generate columnar lattices wherein each column functions as a nanosized wire. The periphery of the dendron serves as an insulator while electrons and holes can pass through the center of the column. The charge carrier mobility obtained is up to 5 orders of magnitude higher than that obtained from the same amorphous polymers.[20]
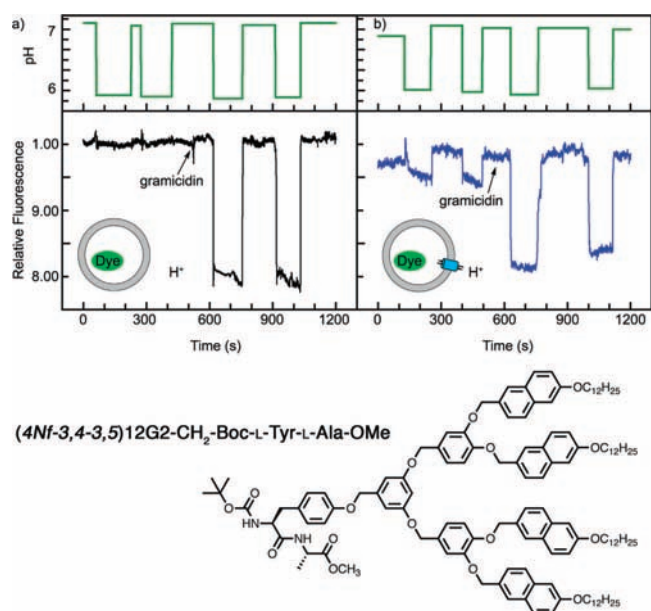
FIGURE 7. Fluorescence assays showing proton transport in pores assembled from **(4Nf-3,4-3,5)12G2-CH₂-Boc-ʟ-Tyr-ʟ-Ala-OMe** reconstituted in phospholipid vesicles: (a) vesicles containing only the membrane-impermeable pH-sensitive dye; (b) vesicles containing the membrane-impermeable pH-sensitive dye and **(4Nf-3,4-3,5)12G2-CH₂-Boc-ʟ-Tyr-ʟ-Ala-OMe**. Reproduced with permission from ref 32. Copyright 2007 American Chemical Society.

Selective Transport by Channel Protein Mimics

Dendronized polymers containing covalent and supramolecular helical backbones have been found to generate porous columnar lattices (Scheme 4 and Figure 6). The pores were identified by a combination of XRD, electron density maps, and transmission electron microscopy (TEM) as low-electron-density regions at the center of the cylindrical object.[25,32] The low-electron-density region penetrates the column length. The channel-like columns have been identified for both dendritic dipeptides[25,27−32] and dendronized *cis*-PPAs.[49,51]

Porous columns formed by dendritic dipeptides have been shown to selectively transport protons and water across a vesicle membrane.[25,32] Quenching of a fluorescent dye in a lipid vesicle as pH is increased only occurs in the presence of pore-forming dendrons or the channel-forming peptide gramicidin A (Figure 7).[25,32] Multinuclear NMR spectroscopy experiments indicate that Li⁺, Na⁺, and Cl⁻ ions are not transported across the phospholipid vesicle.[32] The dendritic dipeptide pores reported thus far can be envisioned as a primitive mimic of aquaporin, which transports water and does not reject protons.

Molecular Nanomachines

Thermoreversible cisoid-to-transoid conformational isomerization of self-organizable dendronized *cis*-PPAs represents a molecular nanomachine: a molecular actuator. The machine is thermally fueled as the transition between the cisoid conformation (i.e., Φ_h^{io} lattice) and the transoid conformation (i.e., Φ_h lattice) is temperature-dependent. XRD demonstrates that the column diameter shrinks upon heating, and modeling confirms that there is a corresponding stretch along the column axis as the backbone adopts the transoid conformation: the helix unwinds (Figure 6). The steric bulk of the dendrons ensures that the motion (extension/contraction) occurs exclusively along the column axis. Thermally fueled, directional motion is achieved by selected examples of self-organizable dendronized *cis*-PPAs. We anticipate that this behavior is not limited to dendronized *cis*-PPAs.

The nanomechanical action undergone by individual cylindrical macromolecules can be harnessed to perform work on macroscopic objects. The orientation of columns within the Φ_h^{io} and Φ_h lattices can be controlled by extruding fiber samples in the liquid crystalline phase. The fibers can be of arbitrary length and diameter. AFM images have shown that the short cylindrical polymers stack end-to-end on highly ordered pyrolitic graphite (HOPG) and mica to form long continuous cylindrical self-assemblies.[60] Similar end-to-end stacking is expected in the fiber and allows the molecular nanomachines to work in concert. On the macroscopic scale, we observe anisotropic extension and contraction of the fibers. Furthermore, we use the work of the nanomachines to displace a dime that weighs 250-times the weight of the fiber (Figure 8).[53]

Outlook

Nature has inspired the design and synthesis of dendronized polymers containing covalent and supramolecular helical backbones. The polymers have confirmed hypotheses previously advanced based on structural and retrostructural analysis of dendronized polymers with flexible backbones. The self-assembling dendrons and dendronized polymers that self-organize into columnar lattices are comprised of helical cylindrical objects. Self-assembling dendrons induce a helical conformation on the backbone penetrating the core of the cylindrical object by increasing the barrier to helix inversion. The objects lack a preferred helical handedness, but this can be selected as shown for dendronized polymers containing helical backbones.

Incorporation of covalent and supramolecular helical backbones into self-organizable dendronized polymers revealed
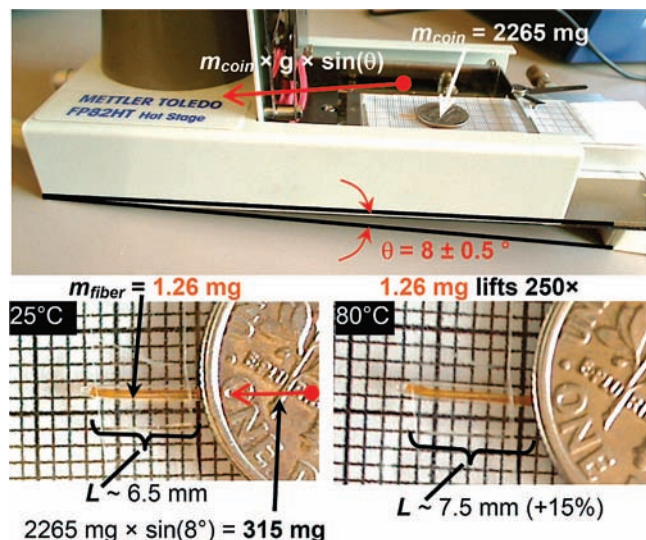
FIGURE 8. Experimental setup that demonstrates the macroscopic scale expansion and contraction of the oriented fiber by the lifting of a dime on the inclined plane of a Mettler hot stage (top). Expanded images collected by a digital camera at 25 °C (bottom left side) and at 80 °C (bottom right side) of the oriented fiber generated from **poly[(3,4-3,5)16G2-4EBn]** during lifting of 250-times its weight via thermally fueled unwinding of its helix at the Φ_h^{io}-to-Φ_h transition. Reproduced with permission from ref 53. Copyright 2008 American Chemical Society.

new structural and functional properties that enable integration of the nanoworld with its macroscopic universe. Porous protein mimics function as selective channels. Molecular nanomachines based on controlled unwinding/winding of the helical backbone can move macroscopic objects. Charge carrier mobility, ionic conductivity, and chemical reactivity were mediated via nanoscale assemblies. All these concepts and strategies provide unprecedented opportunities to interface nanoscale objects and their functions with macroscopic components.

BIOGRAPHICAL INFORMATION

Jonathan G. Rudick received his Ph.D. from the University of Pennsylvania (2005) with Virgil Percec. He was a scientist at Procter & Gamble and is now a postdoctoral researcher with William F. DeGrado at Penn.

Virgil Percec defected from his native country Romania in 1981 and shortly thereafter joined the Department of Macromolecular Science at Case Western Reserve University (1982) as an Assistant Professor. He was promoted to Associate Professor in 1984, to Professor in 1986, and to Leonard Case Jr. Chair in 1993. In 1999, he moved to the University of Pennsylvania as P. Roy Vagelos Professor of Chemistry. Percec's research interests lie at the interface between organic, bioorganic, supramolecular, and polymer chemistry and liquid crystals where he contributed over 590 refereed publications, 46 patents and over 1000 endowed and invited lectures. His list of awards includes Honorary Foreign Member to the Romanian Academy (1993), Humboldt Award (1997), NSF Research Award for Creativity in Research (1990, 1995, 2000), PTN Polymer Award from The Netherlands (2002), the ACS Award in Polymer Chemistry (2004), the Staudinger-Durrer Medal from ETH (2005), the H. F. Mark Medal from the Austrian Research Institute for Chemistry and Technology (2008), and the International Award of the Society of Polymer Science from Japan (2008). He is a Fellow of IUPAC (2001), PMSE Division of ACS (2003), and AAAS (2004). He is the editor of the *Journal of Polymer Science, Part A: Polymer Chemistry* (since 1996) and serves on the Editorial Boards of 20 international journals.

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