Helical chirality in dendronized polyarylacetylenes†

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Dendronized polymers are an archetypal polymer architecture upon which new concepts for single-molecule and bottom-up self-assembly of nanotechnologies can be derived. Helical order and control of its screw sense within the cylindrical macromolecules promises to enhance the utility of these building blocks. Herein we summarize efforts to program the handedness of helical, self-organizable dendronized polyarylacetylenes as well as of related dendronized polymers.

Introduction

Dendronized polymers, which possess a dendritic side chain on (essentially) every repeat unit of a polymer backbone, have emerged as powerful building blocks for nanoscience.[1–3] Discrete cylindrical and spherical structures with well-defined dimensions can be prepared and manipulated individually.[2–7] Alternately the objects can self-organize into periodic arrays or lattices.[2–4,8–17] Consequently, dendronized polymers are an archetypal polymer architecture from which new concepts for single-molecule and bottom-up self-assembly of nanotechnologies can be derived.[1–3,14,18,19]

Synthetic strategies toward dendronized polymers have expanded to include four unique approaches. Tomalia and co-workers[20] pioneered the divergent growth strategy whereby a linear polymer core is used to initiate the first generation of dendritic growth. Subsequent iterations increase the generation of the dendritic side chains. The advent of the iterative

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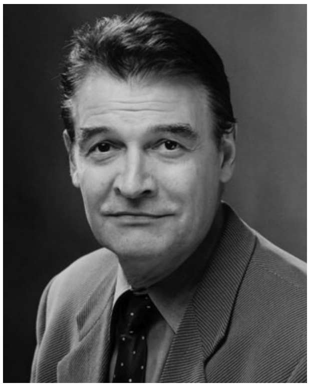

Professor Virgil Percec was born and educated in Romania (PhD in 1976 with C. I. Simionescu at the Institute of Macromolecular Chemistry in Jassy). In 1981 he defected from his native country and after short postdoctoral stays at the University of Freiburg in Germany (with H.-J. Cantow) and University of Akron (with J. P. Kennedy) he joined the Department of Macromolecular Science of Case Western Reserve University in 1982 as an Assistant Professor. He was promoted to Associate Professor in 1984 and to Professor in 1986. In 1993 he was awarded the Leonard Case Jr. Chair at Case Western Reserve University and in 1999 he moved to the University of Pennsylvania as P. Roy Vagelos Professor of Chemistry.

He has been repeatedly a visiting professor at the Universities of Freiburg, Ulm and at the Max Planck Institute for Polymer Research in Mainz (all in Germany) and at the Royal Institute of Technology in Stockholm.

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) and the Staudinger–Durrer Medal from ETH (2005). He is a Fellow of IUPAC (2001), PMSE Division of ACS (2003) and AAAS (2004).

Percec chaired and organized numerous symposia including the US–Japan Seminar on Polymer Synthesis (1993), the first European (1997) and the US (1998) Gordon Research Conferences on Polymers and the 35th International IUPAC Symposium on Macromolecules (1994).

Percec's research interest is at the interface between organic, supramolecular, polymer chemistry and liquid crystals where he contributed over 580 refereed publications, 36 patents and over 1000 endowed and invited lectures including the Woodward Lecturer 'Frontiers in Chemical Sciences' at Harvard University (2004) and the Rohm and Haas Lecture at UC Berkeley (2005). He is the editor of the Journal of Polymer Science, Part A: Polymer Chemistry (since 1996) and serves on the Editorial Boards of 20 other international journals.

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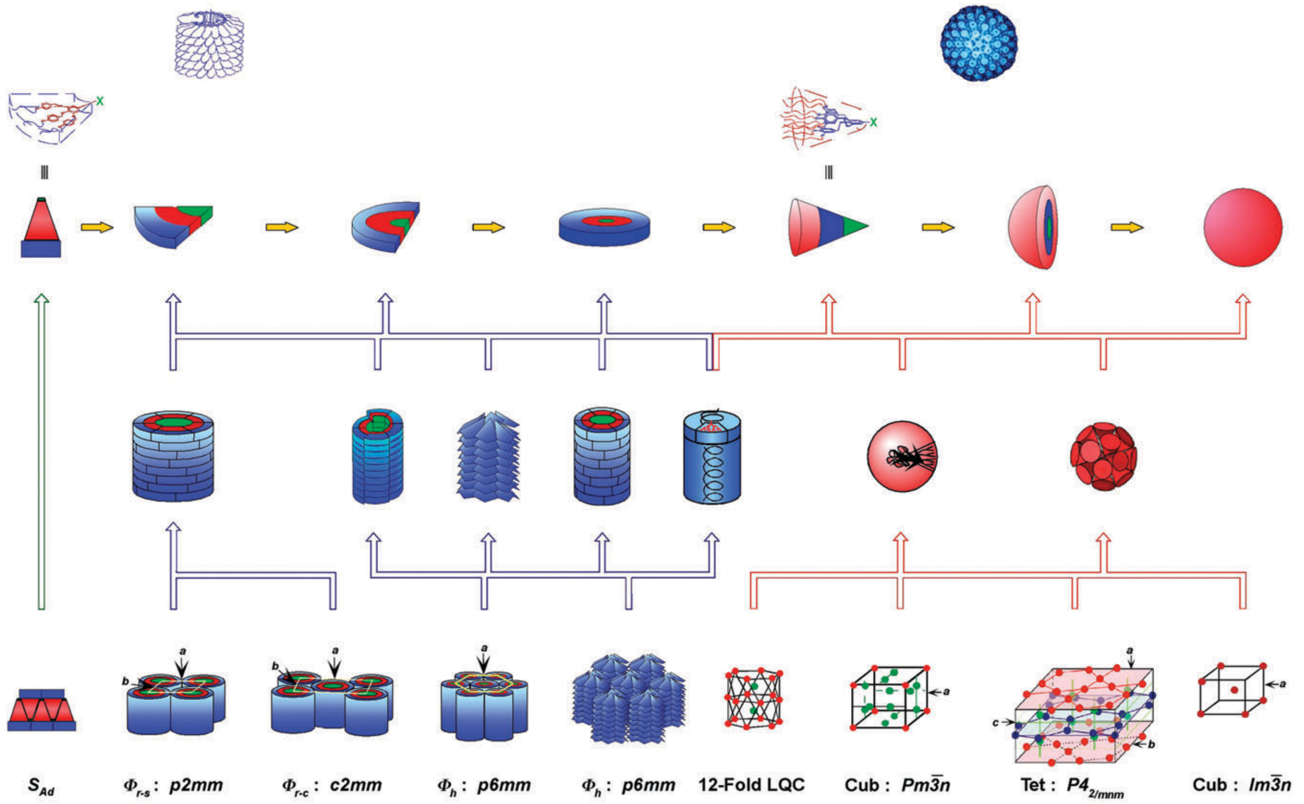


Scheme 1

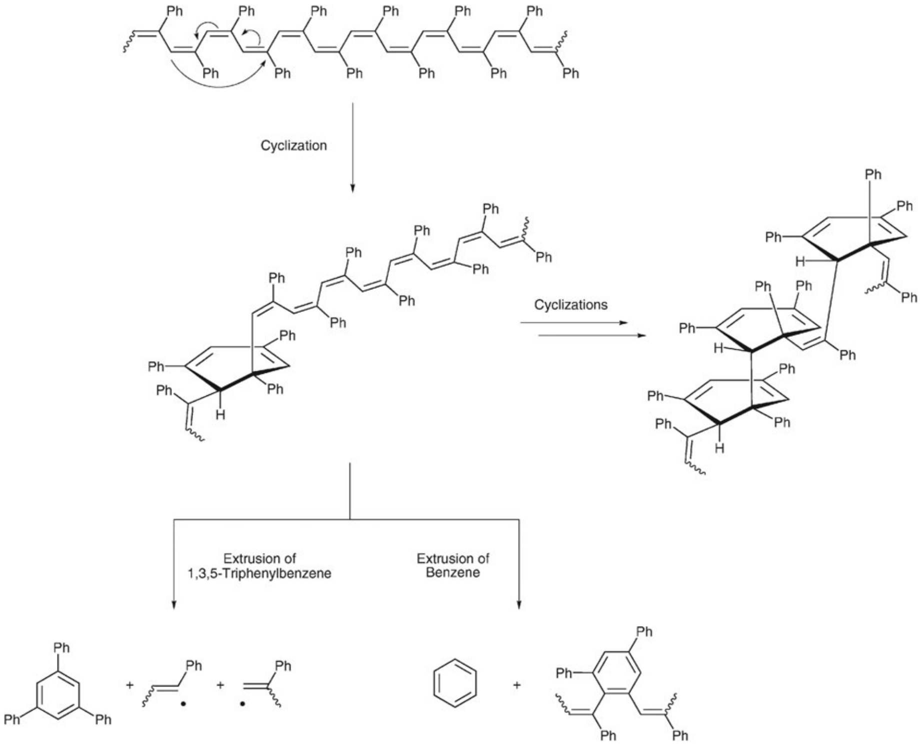
convergent synthesis of dendrons and dendrimers[21] introduced by Hawker and Fréchet made two additional strategies possible. The attach-to strategy combines preformed linear polymer cores and preformed dendrons. We had used such an approach with first-generation self-assembling dendrons,[2,22] and, later, Schlüter and co-workers extended this approach using higher generation Fréchet-type dendrons.[5,23]

The third approach to dendronized polymers involves polymerization of dendritic monomers; the so-called macromonomer strategy.[1,5] Hawker and Fréchet copolymerized third-, fourth- and fifth-generation dendritic styrenes with styrene by free radical initiation.[24] At about the same time, we demonstrated radical polymerization of first-generation methacrylate monomers[25] and living cationic polymerization of first-generation vinyl ether monomers.[26] Homopolymers from second-,[27] third-,[28] and fourth-generation[6,29] dendritic macromonomers have subsequently been shown to be possible, though not trivial.

Most recently, a supramolecular attach-to strategy has been introduced.[18] Non-covalent association of electron donor or acceptor polymers with semifluorinated dendrons containing complimentary acceptor or donor groups at their apex form dendronized polymer wires that exhibit exceptionally high charge carrier mobility in their self-organized lattices.[18] A similar use of non-covalent association has been subsequently reported by others.[30,31]

Self-organization, the spontaneous generation of periodic order under a given set of conditions,[32] reflects emergent complexity in supramolecular assemblies and enables their investigation *via* retrostructural analysis (Scheme 1).[4,10,11,13–18,22,25,26,33–38] Self-assembling dendrons are those fragments of a dendrimer capable of spontaneously forming well-defined supramolecular assemblies either in bulk or solution. As illustrated in Scheme 1, we have discovered self-assembling dendrons[33–36] whose supramolecular assemblies possess the structural perfection necessary for self-organization in smectic, two-dimensional (2D) columnar lattices with simple rectangular ($\Phi_{r\text{-}s}$), centered rectangular ($\Phi_{r\text{-}c}$) or hexagonal (Φ_h) symmetry, and three-dimensional (3D) arrays with cubic, tetragonal,[34] or 12-fold liquid quasicrystalline[35] periodic and quasiperiodic order. Such ordered arrays facilitate their structural and retrostructural analysis (Scheme 1) using a combination of techniques elaborated in our laboratory.[33–36] Lattices of electronic materials[18] and helical dendritic dipeptide nanopores[36] have introduced powerful new concepts for self-assembled supramolecular materials. We have developed and exploited the use of self-assembling dendrons[33–36] as a strategy to reliably prepare self-organizable dendronized polymers.[4,10,11,13–18,22,25,26,37,38]

Control of internal order within the macro- or supramolecular objects that comprise the array promises to improve previously identified functions and impart wholly new properties. For example, selection of a single helical handedness within columnar arrangements of organic electronic materials[18,39] is anticipated to enhance charge carrier mobility. One strategy to successfully dictate internal structural order has been through apical chirality in dendritic dipeptides.[36] Choice of N- and C-terminal functionality, amino acid chirality,



Scheme 2

amino acid sequence, and dendron structure all can be used to tailor the properties of helical porous columns.[36] An alternate approach has been to rely on side chain chirality to bias the helical handedness of helix forming polymers.[13–16]

Polyarylacetylenes, of which polyphenylacetylene (PPA) is the simplest example, can include either of four stereo- and conformational isomers: *cis*-cisoidal, *cis*-transoidal, *trans*-cisoidal, and *trans*-transoidal. Helical conformations for each of the four isomers had been identified by Simionescu, Percec, and co-workers as part of the earliest efforts to structurally characterize PPA.[40] At the same time, these authors identified structural instability in the polyene backbone in polyarylacetylenes (Scheme 2).[40] Briefly, 6π-electrocyclization along the polyene backbone produces 1,3-cyclohexadiene defects.[40–44] This process is thermally activated, occurs in the absence of oxygen and light, and does not invoke the formation of radical species.[40–44] Once formed, the 1,3-cyclohexadiene units can rearomatize to extrude triphenylbenzene.[40–44] This process appears to have a much higher activation energy. Both cyclization and rearomatization are accelerated by the presence of even trace amounts of acid.[43] Additionally, oxidative cleavage of the polyene backbone has been identified only in the presence of both light and oxygen (*i.e.*, an apparent photooxidative process). Each of these events results in varied degrees of change in polymer molecular weight.

Helix sense selection in polyarylacetylenes[45] has confirmed the helical conformation of *cis*-transoidal PPA proposed by Simionescu, Percec, and co-workers.[40] The handedness of the helical conformation can be dictated by incorporation of chiral, non-racemic side chains,[46] non-covalent association of chiral, non-racemic analytes,[47,48] or by helix sense selective polymerization in the presence of chiral, non-racemic co-catalysts.[49] While very few reports of these phenomena consider the implications of the aforementioned structural transformations in polyarylacetylenes, we have shown for (−)-poly[4-(L-menthyloxycarbonyl)phenylacetylene] that 6π-electrocyclization along the polyene backbone leads to a decrease in the observed signal in circular dichroism (CD) spectra.[44]

The conjugated PPA backbone allows us to directly interrogate its conformation in solution by CD and UV-Vis spectroscopies, which can be further combined with bulk characterization using CD and UV-Vis spectroscopies, X-ray diffraction (XRD), and atomic force microscopy (AFM) visualization. We aim to elucidate the principles for transmission of chiral information as it relates to bio-inspired supramolecular materials. The steric bulk and regularly repeating dendron structure are used to create single molecule nanostructures. Furthermore, it is envisioned that the dendrons will enable self-organization of the cylindrical macromolecules and potentially inhibit structural transformations due to intramolecular cyclization of the polyene backbone.

Herein we discuss our continued effort to elucidate strategies for the control of the helical internal order in cylindrical dendronized polyarylacetylenes.[13–17] Where possible we include relevant discussion of other examples of dendronized polyarylacetylenes.[31,50–55] We will discuss the synthesis, structural and retrostructural analysis of self-organizable dendronized polyarylacetylenes. We have identified helical order within these polymers and generalized the helical conformation found here for other polymers dendronized with self-assembling dendrons. A unique structural model for steric communication of peripheral chiral information to the polymer backbone has been elucidated. Preliminary observations for stabilization against thermal transformations in PPAs and gating of a porous cylindrical macromolecule serve as the bases for the future outlook for these novel macromolecules.

Synthesis of dendronized polyarylacetylenes

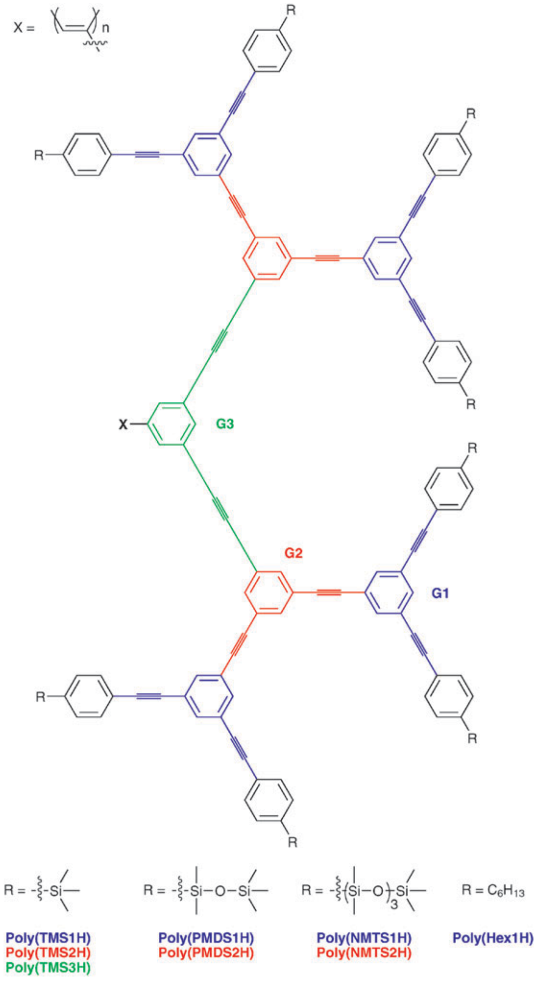
Arylacetylenes are commonly polymerized using Ziegler–Natta catalysts,[40] metathesis catalysts,[41] and rhodium-based 1,2-insertion polymerization catalysts.[13–17,42–44,50–59] Rhodium-based catalysts are stereospecific for *cis*-transoidal polymers and highly tolerant of functional groups.[56] Furthermore, Noyori and co-workers have developed a rhodium-based catalyst for living polymerization of arylacetylenes.[59]

In all but one example[31] dendronized polyarylacetylenes have been prepared by the so-called macromonomer approach using rhodium-based catalysts.[14–17,50–55] Dendritic arylacetylene monomers with first-generation self-assembling dendrons[15,16,55] as well as first-, second-, and third-generation phenylene ethynylene dendrons[50–54] are readily polymerized using $[Rh(nbd)Cl]_2/NEt_3$ (nbd = 2,5-norbornadiene) as a catalyst (Schemes 3, 4 and 5). A few other types of dendrons have been used to prepare dendronized PPAs (Schemes 4 and 5).[53,54] High molecular weight *cis*-transoidal dendronized PPAs have been prepared in this manner.

An apparent limitation of $[Rh(nbd)Cl]_2$ as a catalyst was observed for first- and second-generation dendrons containing benzyl ether moieties.[15] In such cases, the reactions fail to reach completion and the products are intractable solids. This may relate to the acid lability of some benzyl ether groups, since poly(MG0PA), poly(HG0PA), poly(HG1PA) and poly (DG0PA) (Scheme 5) were prepared using $[Rh(nbd)Cl]_2/NEt_3$.[53]

Fortunately, this side reaction can be circumvented in many instances using Noyori's catalyst for living polymerization of arylacetylenes, $Rh(C{\equiv}CPh)(nbd)(PPh_3)_2$/DMAP (DMAP = 4-*N*,*N*-dimethylaminopyridine).[59] A series of dendronized poly(ethynylcarbazole)s[13] (Scheme 6) and a library of dendronized PPAs[14,15,17] (Scheme 7) have been prepared this way. Demonstration that the polymerization possesses living character was obtained through kinetic analysis of the polymerization and linear increase of molecular weight with [monomer]/[Rh].[15]

Two caveats need to be considered with regard to the general success of the living polymerization of dendritic arylacetylene monomers. First, dilute reaction conditions are used to ensure that the reaction mixtures are homogeneous and highly fluid (*i.e.*, not viscous) throughout the reaction. Consequently, broadening of the molecular weight distribution is observed. This is likely due to 6π-electrocyclization along the polyene backbone. Second, competing side reactions that are kinetically insignificant for small dendritic monomers can become significant for very large dendritic monomers.[37] The apparent rate of propagation decreases with increasing size of the dendritic monomer. Undesirable side reactions (*e.g.*, chain termination or benzyl ether cleavage noted above) might occur when the monomer concentration becomes too low or when the dendritic monomer is too large.



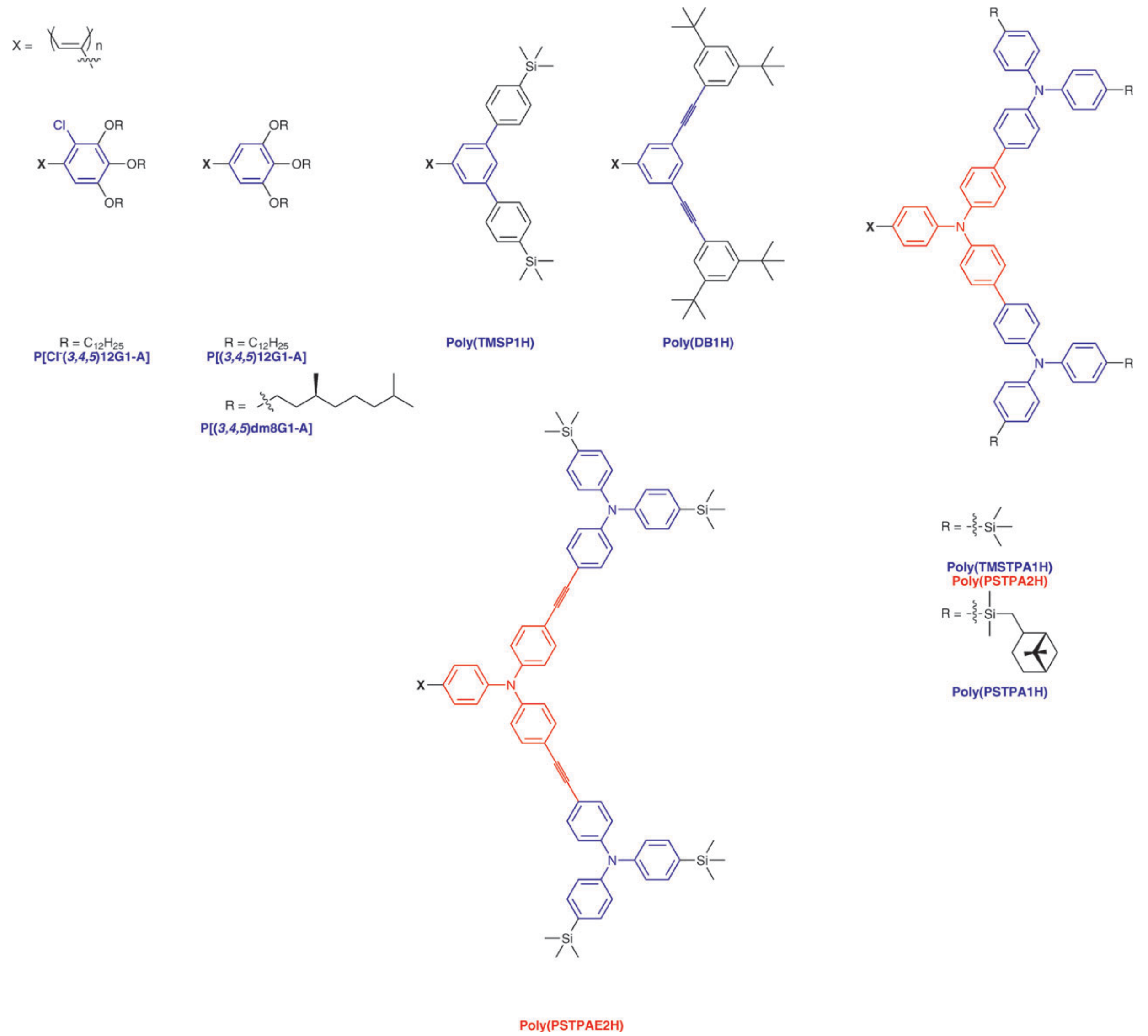
Scheme 3

An example of the supramolecular attach-to strategy to prepare dendronized PPAs has also been reported.[31] Yashima, Kato, and co-workers prepared three *para*-substituted PPAs that contain acidic functional groups using Rh-based catalysts in combination with a base.[31,57,58] First- or second-generation self-assembling glutamic acid dendrons with varied stereochemical composition and an amine at their apex were used to form dendronized PPAs *via* acid–base interactions (Scheme 8).[31] In all cases, the dendron was used in excess relative to the number of arylacetylene repeat units. Due to the dynamic nature of the structure in solution, it is difficult to assess the degree of structural perfection achieved.

Structural and retrostructural analysis of dendronized polyarylacetylenes

Dendronized polyarylacetylenes in solution

While Rh-based catalysts are known to promote stereoselective polymerization of monosubstituted arylacetylenes high *cis*-content should not be taken as a foregone conclusion. Methods for the identification and quantification of *cis*-content in PPA have been developed in our group using NMR

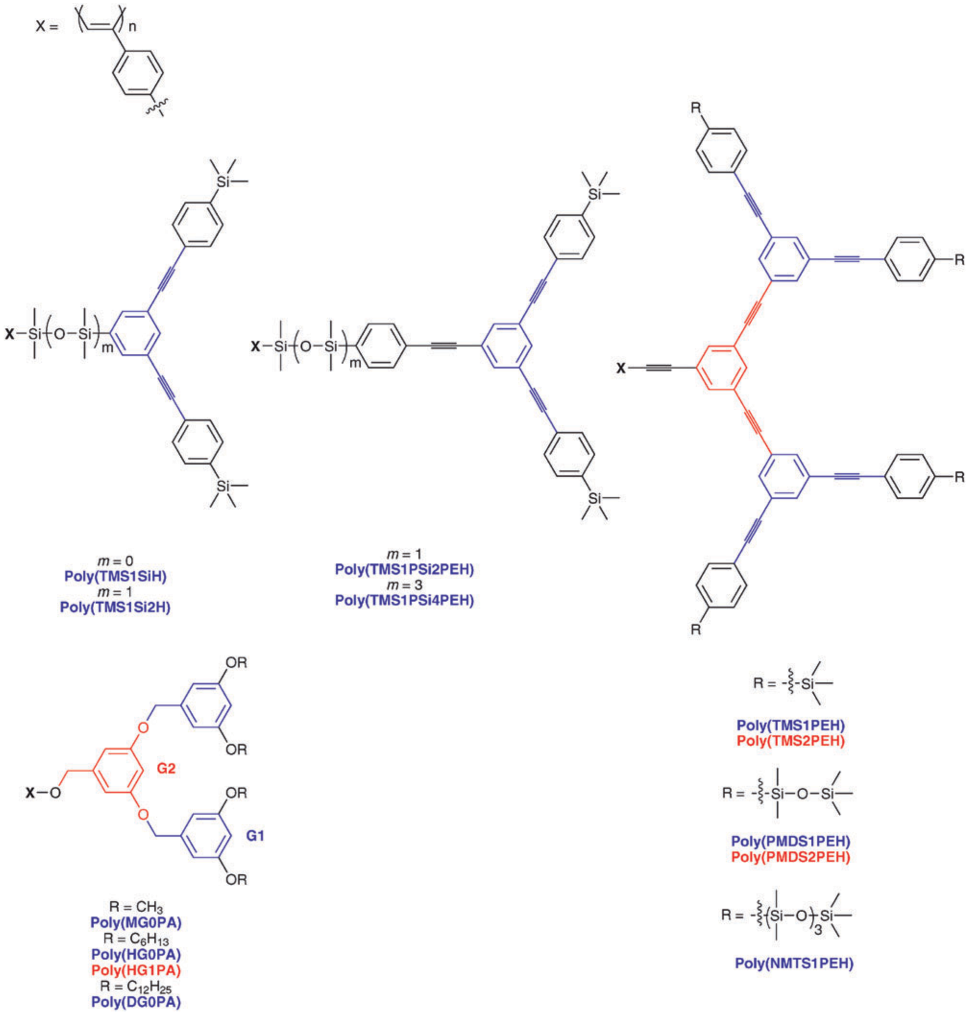


Scheme 4

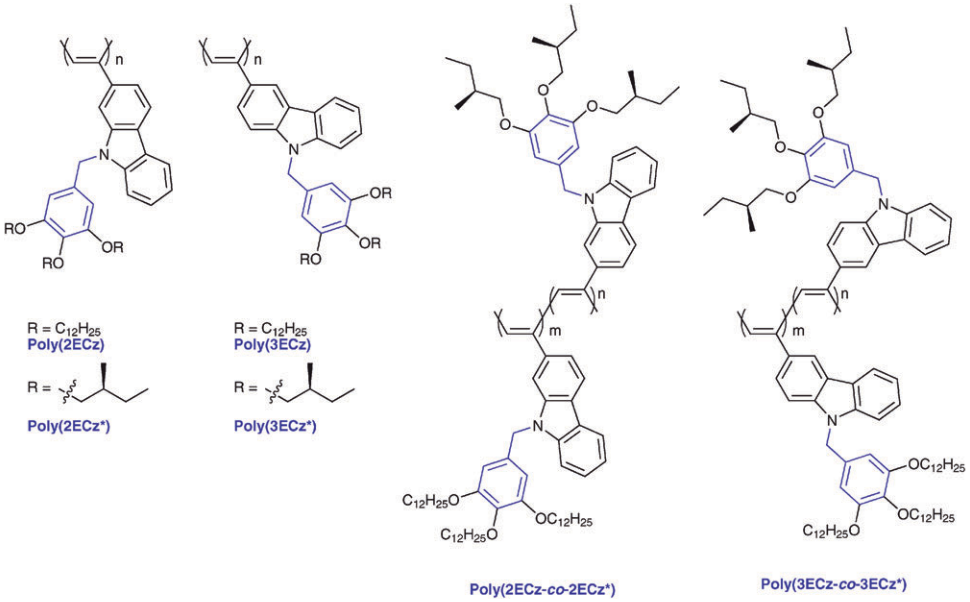
spectroscopy as the primary tool.[40–43] IR Spectroscopy is less reliable for quantification of *cis*-content since it requires calibration using ^{1}H NMR spectroscopy.[40] Two methods have been used to assess the *cis*-content from ^{1}H NMR spectra based on the *cis*-polyene proton resonance at $\sim\delta$5.8 ppm.[40–43] The simpler approach compares the integrated intensity of the *cis*-polyene resonance *vs.* the full spectrum because the *trans*-polyene proton resonance is overlapped by the aromatic resonances.[40,42] A more rigorous approach accounts for the formation of 1,3-cyclohexadiene sequences along the polyene backbone due to 6π-electrocyclization.[41]

All existing reports of the *cis*-content of dendronized polyarylacetylenes utilize the simpler of the two aforementioned methods. In the case of PPA dendronized with self-assembling dendrons, it was not possible to discern the methine proton resonance of 1,3-cyclohexadiene sequences due to overlap by the alkyl ether methylene resonances of the peripheral chains.[14–16,55] As determined, polymers with *cis*-content $>85\%$ were readily obtained.[14–16,55] For the dendronized poly(ethynylcarbazole)s the *cis*-polyene proton resonance was overlapped by the aromatic proton resonances making it impossible to assess any measure of *cis*-content.[13] The *cis*-content for PPA dendronized with phenylene ethynylene dendrons was not reported, but the reported data suggest that it should be possible to determine the *cis*-content and account for the formation of 1,3-cyclohexadiene sequences. Nonetheless, we stress that Rh-catalyzed polymerization of arylacetylene monomers is not typically complicated by formation of 1,3-cyclohexadiene sequences.[43]

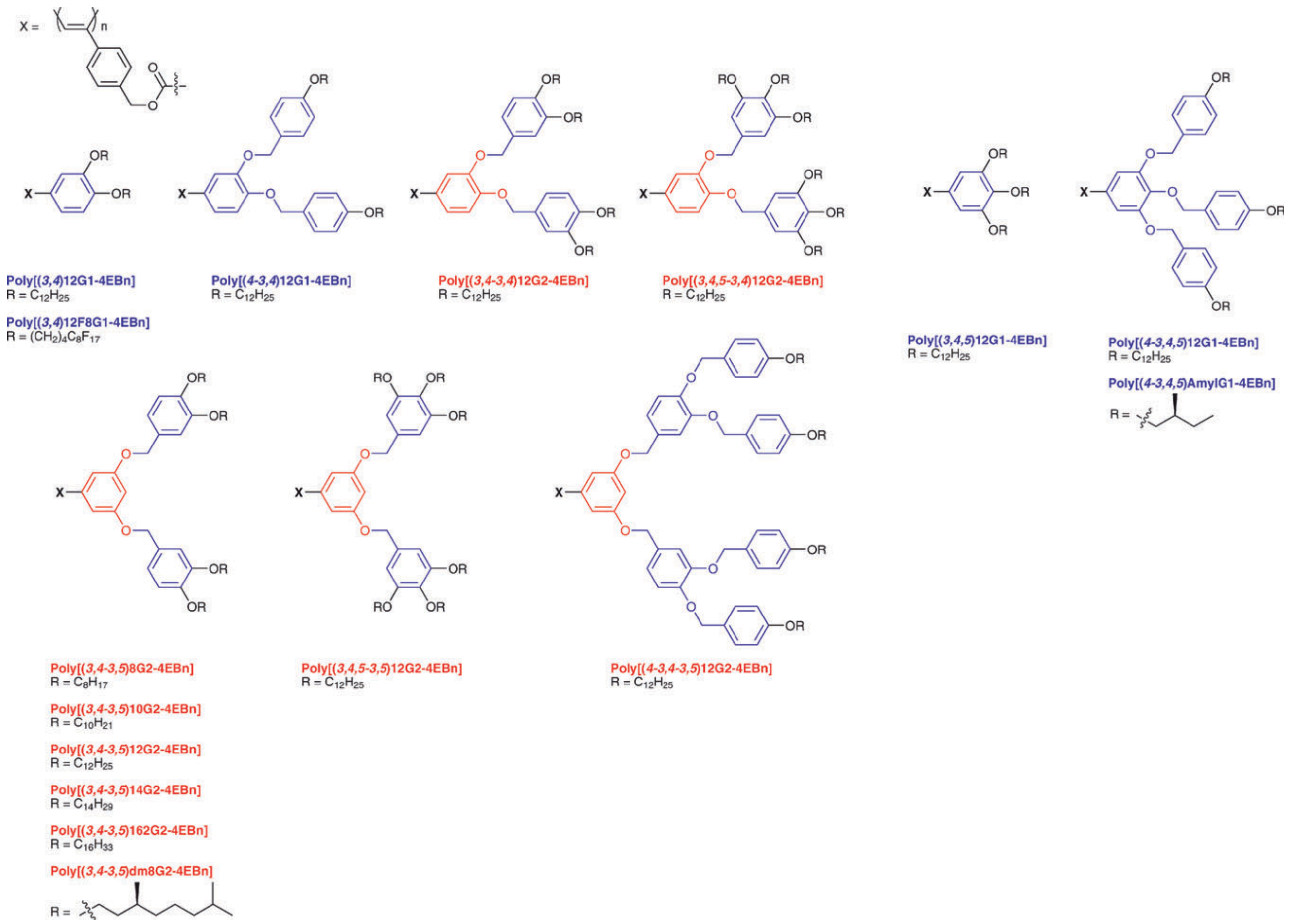
In addition to the *cis*-content, conjugation along the polyene backbone is indicative of how stretched or compressed is the helical polymer (*i.e.*, *cis*-transoidal *vs.* *cis*-cisoidal). It might be anticipated that the steric bulk of the dendritic side chains stretches the polymer and leads to greater conjugation along the polyene backbone. UV-Vis Spectroscopy has been used to investigate this concept with varied results.



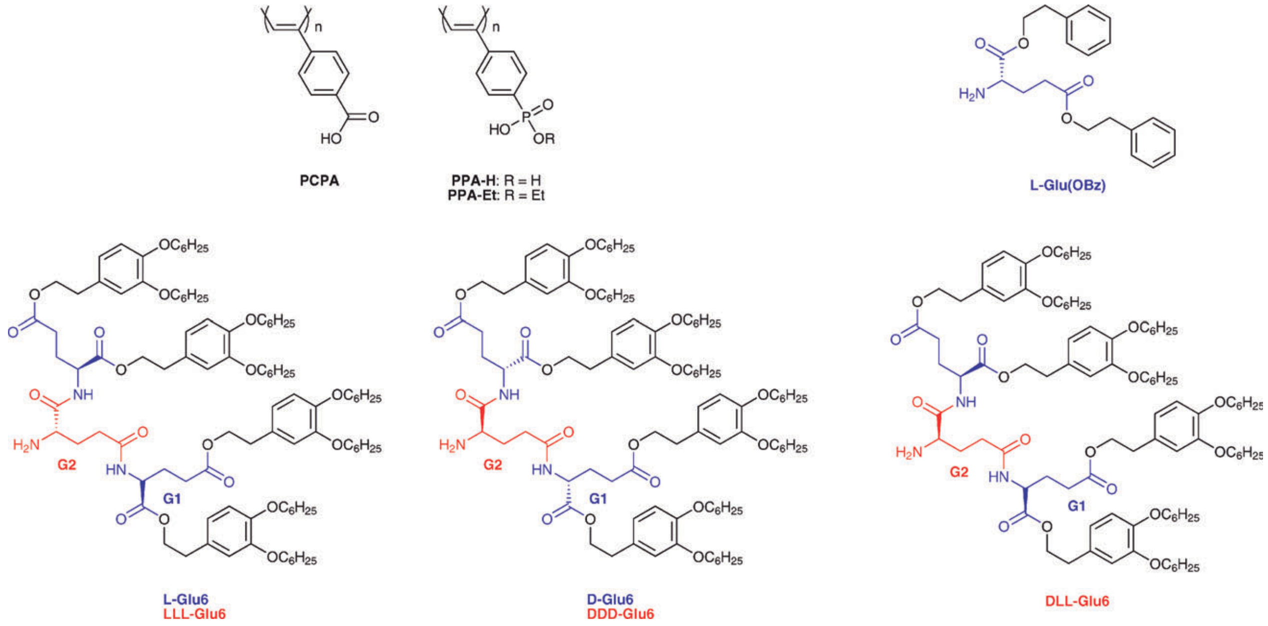
Scheme 5



Scheme 6



Scheme 7



Scheme 8

For PPA dendronized with phenylene ethynylene dendrons, there is a clear red shift of the long wavelength absorption upon increasing the size of the dendron from a model "zeroeth-generation" polymer to poly(TMS1H), and then to poly(TMS2H).[50–54] This is consistent with the dendron forcing the backbone to stretch its conformation. Surprisingly, poly(TMS3H) exhibits a very weak absorption in this region with no observed maximum or cutoff up to 600 nm.[51–54] The orange color reported for films of poly(TMS3H)[52] suggest that this absorption is not negligible though its origin is not self-evident.

Self-organizable dendronized PPAs exhibit different behavior. In a given solvent (*e.g.*, THF or hexanes) the long wavelength absorption of these polymers is invariant over the range of dendrons employed.[14–16,55] The absorption maximum in the backbone region of the spectrum is red shifted 15–20 nm upon going from THF to hexanes as solvent.[15] This is likely related to solvophobic collapse of the benzyl ether portion of the dendrons. In a manner analogous to the role of water in protein folding, solvents selective for the peripheral alkyl chains meditate intramolecular folding of the dendrons into well-defined supramolecular structures. In this more compact conformation, the dendrons apparently occupy a larger volume and result in some stretching of the polyene backbone.

In further contrast to PPA dendronized with phenylene ethynylene dendrons, a blue shift is observed in the UV-Vis spectra of the supramolecular dendronized PPAs upon increasing generation of the dendron in DMSO–$CHCl_3$ (66 : 34 v/v).[31] The authors note that this suggests a more compact chain conformation. When dendrons are covalently attached to the polymer backbone, significant stretching of the backbone can occur due to the steric demands of the adjacent dendrons.[4,5,7] In a dynamic system it is reasonable that steric interactions between adjacent dendrons can preclude 1 : 1 association. To compensate, the PPA chain might collapse to maximize interactions between a single dendron apex and multiple acid functionalities.

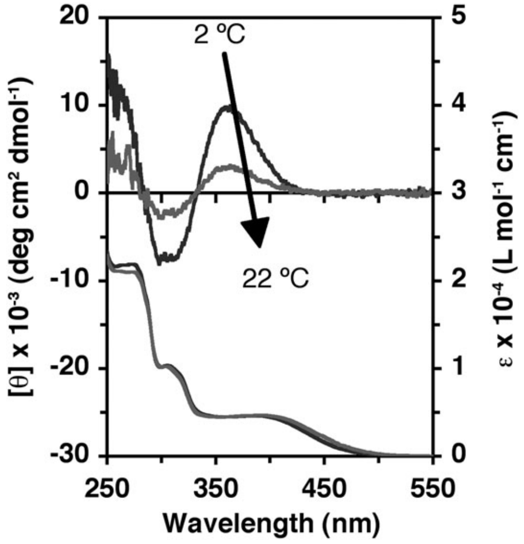


Fig. 1 Circular dichroism (top, left axis) and UV-Vis spectra (bottom, right axis) of poly[(*3,4-3,5*)dm8G2-4EBn] in methyl cyclohexane ([4EBn] = 9.1 × 10^{-4} M) at 2 °C and 22 °C. (Reprinted with permission from ref. 14. Copyright 2005, American Chemical Society.)

In the dendronized poly(ethynylcarbazole) series we observe several significant changes of the backbone absorption in the UV-Vis spectrum in hexanes due to changes in the repeat unit structure. Regardless of the peripheral alkyl chains, the dendronized poly(2-ethynylcarbazole)s are red shifted compared to the corresponding dendronized poly(3-ethynylcarbazole)s.[13] Upon changing the peripheral alkyl chains from dodecyl to (*S*)-amyl the same absorption is blue shifted 20–25 nm.[13] The poly(2ECz-*co*-2ECz*) copolymers display a gradual progression through this blue shift with increasing amounts of 2ECz* repeat units. In contrast, no blue shift is observed in any of the poly(3ECz-*co*-3ECz*) copolymers relative to poly(3ECz*).

Much of the above results can be explained by the collapsed state of the dendronized polyarylacetylene in a poor solvent for the aromatic portion of the polymer. Longer alkyl chains more effectively shield the aromatic core, thus requiring less collapse of the polymer. Additionally, the differences between the 2-ethynyl- and 3-ethynylcarbazole polymers suggest that the latter aromatic side chains pack more tightly. This is not the only contributing factor, though, as seen from the differing behaviors of the two different series of copolymers, poly(2-ECz-*co*-2ECz*) and poly(3ECz-*co*-3ECz*).

CD spectroscopy was used to explore helix sense selection by peripheral chiral tails in self-assembling dendrons. Meijer and co-workers first showed that peripheral (*S*)-3,7-dimethyloctyl (dm8) tails resulted in a strong CD signal in *o*-dichlorobenzene associated with the polyene backbone for poly[(*3,4,5*)dm8G1-A].[55] Percec, Meijer, and co-workers have shown this also to be true in methyl cyclohexane, a solvent selective for the peripheral alkyl tails.[16] The chiral homopolymers poly(2ECz*) and poly(3ECz*) also exhibit strong CD signals associated with the polyene backbone.[13] This clearly demonstrated the potential to bias the helical screw sense of the polyene backbone in a *cis*-PPA and other polyarylacetylenes. Remarkably, helix sense selection by chiral tails on a second generation dendronized PPA has also been observed for poly[(*3,4-3,5*)dm8G2-4EBn] (Fig. 1).[14]

CD spectra of the poly(ethynylcarbazole) copolymers[13] revealed differing magnitude sergeants-and-soldiers effect.[60,61] Only for large amounts of chiral comonomer in poly(2ECz-*co*-2ECz*) (F^* = 0.8) is a CD signal observed, while for poly(3-ECz-*co*-3ECz*) there is an observable signal in the CD spectrum at low amounts of chiral comonomer (F^* = 0.2).[13] Recall that the chain length effect on the UV-Vis spectra for dendronized poly(ethynylcarbazole)s was gradual for the 2-ethynylcarbazole polymers yet sudden for the 3-ethynylcarbazoles. Since the ability of a single chiral repeat unit to direct its achiral neighbors is directly related to the population of helix reversals,[61] we might consider that the relative extension of the dendronized 2-ethynylcarbazoles compared to the dendronized 3-ethynylcarbazoles observed by UV-Vis spectroscopy is due, in part, to the frequency of helix reversals.

In *o*-dichlorobenzene, poly[(*3,4,5*)dm8G1-A] apparently undergoes reversible, thermally-induced stereomutation as demonstrated by an inversion of the CD signal during heating/cooling cycles. The thermally-induced CD spectral changes observed for poly[(*3*,*4*,*5*)dm8G1-A][55] are remarkably different than for (−)-poly[4-(L-menthyloxycarbonyl)phenylacetylene].[44] Thus it is unclear what (if any) role thermal transformations of PPA might play in thermally-induced stereomutation.

A predominant helical handedness is obtained from supramolecular dendronized PPAs, as well.[31] While a stronger CD signal is obtained for second-generation dendrons compared to first-generation dendrons, the sign of the observed Cotton effect appears to be dictated solely by the chirality of the apex.[31] The authors suggest that the larger dendrons induce a greater excess of a single-handed helical conformation.[31] The unknown stoichiometry of the complex and apparent change in conformation when the dendron size changes make it difficult to describe a structural basis for such a phenomenon.

Investigation of dendronized polyarylacetylenes in solution has elucidated several parameters by which to control the molecular and conformational structure. Synthetic strategies relying upon Rh-based catalysts provide a general route to high *cis*-content polymers. Use of Noyori's catalyst for living polymerization of arylacetylene monomers[59] provides predictive control over molecular weight and narrow molecular weight distribution. Choice of dendritic side chains (*i.e.*, flexibility and size) has the greatest impact on the polymer conformation in solution due to steric effects. In the case of self-assembling dendritic side chains, the choice of peripheral tails impacts the conformational properties of the polyene backbone, especially in solvents selective for only one portion of the dendron. The presence of chiral, non-racemic groups in the dendron has a relatively modest impact on the overall polymer conformation. Finally, packing of the aromatic substituent adjacent to the polyene backbone leads to distinct differences in how well the polymer adopts more compact helical conformations.

Retrostructural analysis of dendronized polyarylacetylenes in bulk

Retrostructural analysis is the process by which we interpolate between bulk self-organized lattices and known molecular structures to characterize constituent elements that comprise the lattice (Scheme 1). In doing so, underlying self-assembly processes can be elucidated. This process utilizes a combination of the molecular characterization tools discussed above with bulk structural analysis tools including differential scanning calorimetry (DSC), thermal optical polarized light microscopy (TOPM), X-ray diffraction, density measurements, transmission electron microscopy (TEM), and electron density mapping. Finally, these experimental results are pooled to construct molecular models that describe self-assembly and self-organization phenomena.

First-generation self-assembling dendrons, or minidendrons, serve as models for the elaboration and elucidation of novel self-assembly processes found in larger dendrons.[10–12,62] This is analogous to simple peptide sequences used to understand molecular engineering principles for assembling more complex protein structures.[63] This has been fruitful for the investigation of dendronized polyarylacetylenes.[13–16,55]

Cylindrical dendronized poly(ethynylcarbazole)s exhibit nematic (N) or chiral nematic (N_C) order in bulk.[13] No transitions were observed by DSC. A *Schlieren* texture with two-brush defects was identified for poly(2ECz) and poly(3ECz) using TOPM, which is indicative of N order. For poly(2ECz*) and poly(3ECz*) N_C order was indicated by a planar texture. These phase assignments were substantiated by XRD. Due to the low degree of order in these systems it was not possible to confirm internal helical order. Nonetheless, expression of the peripheral chirality is clearly evidenced by the N_C phase assignments for poly(2ECz*) and poly(3ECz*).

Greater structural detail has been determined from PPAs dendronized with self-assembling dendrons.[14–16,55] In all cases these cylindrical macromolecules self-organize into 2D or 3D columnar lattices although no diagnostic textures were found using TOPM.[14–17,55] Columnar hexagonal (Φ_h),[14–17,55] internally-ordered hexagonal columnar ($\Phi_\mathrm{h}^\mathrm{io}$),[14,15] simple rectangular ($\Phi_\mathrm{r\text{-}s}$),[15] and 3D centered rectangular ($\Phi_\mathrm{r\text{-}c,k}$)[16] lattices have all been confirmed by XRD. The ability to vary the diameter of the cylindrical PPAs through the length of the peripheral alkyl tails,[14] the dendron generation,[15] or the dendron substitution pattern[15] was confirmed.

Transition temperatures and corresponding enthalpies determined by DSC for P[(*3*,*4*,*5*)dm8G1-A] are notably lower than for either P[(*3*,*4*,*5*)12G1-A] or P[Cl-(*3*,*4*,*5*)12G1-A]. Such is expected when branching in the peripheral tails disrupts packing during crystallization. Interestingly, higher transition temperatures and corresponding enthalpies are observed for P[Cl-(*3*,*4*,*5*)12G1-A] *vs.* P[(*3*,*4*,*5*)12G1-A]. This is possibly a result of increased polarity due to the additional chlorine atom.

Wide angle XRD experiments on oriented fiber samples confirmed helical order in several dendronized PPAs with achiral peripheral tails,[14–16] as well as in those with chiral, non-racemic alkyl tails[14–16,55] for which CD spectroscopy had revealed helix sense selection in solution. This indicates the key distinction between helicity induction[31,48,58] and helix sense selection.[61] Helicity is induced when a polymer adopts a non-helical conformation in an achiral or chiral, racemic environment, but adopts a helical conformation in a chiral, non-racemic environment. If the polymer adopts a helical conformation in achiral or chiral, racemic environments, then the predominant helical handedness is selected by the chiral, non-racemic environment. Clearly, for dendronized PPAs it is most appropriate to categorize the CD spectral responses described above as helix sense selection, since a helical conformation is found even in polymers that are optically inactive.

In the poly[(*3*,*4*-*3*,*5*)*m*G2-4EBn] series of dendronized PPAs there is a reversible thermal transition between the $\Phi_\mathrm{h}^\mathrm{io}$ (*i.e.*, lower temperature) and Φ_h (*i.e.*, higher temperature) phases observed by DSC.[14] Furthermore, a porous feature similar to that in self-assembled dendritic dipeptides[36] was identified in a reconstructed electron density map from XRD data for poly[(*3*,*4*-*3*,*5*)12G2-4EBn] in the $\Phi_\mathrm{h}^\mathrm{io}$ phase at 50 °C.[14] XRD patterns obtained through the $\Phi_\mathrm{h}^\mathrm{io}$-to-$\Phi_\mathrm{h}$ transition reveal a discontinuous change of the column diameter.[14] In the higher temperature phase the helical and porous features are no longer identifiable.[14] Fig. 2 illustrates a model for the porous and non-porous helical cylindrical PPAs, as well as the

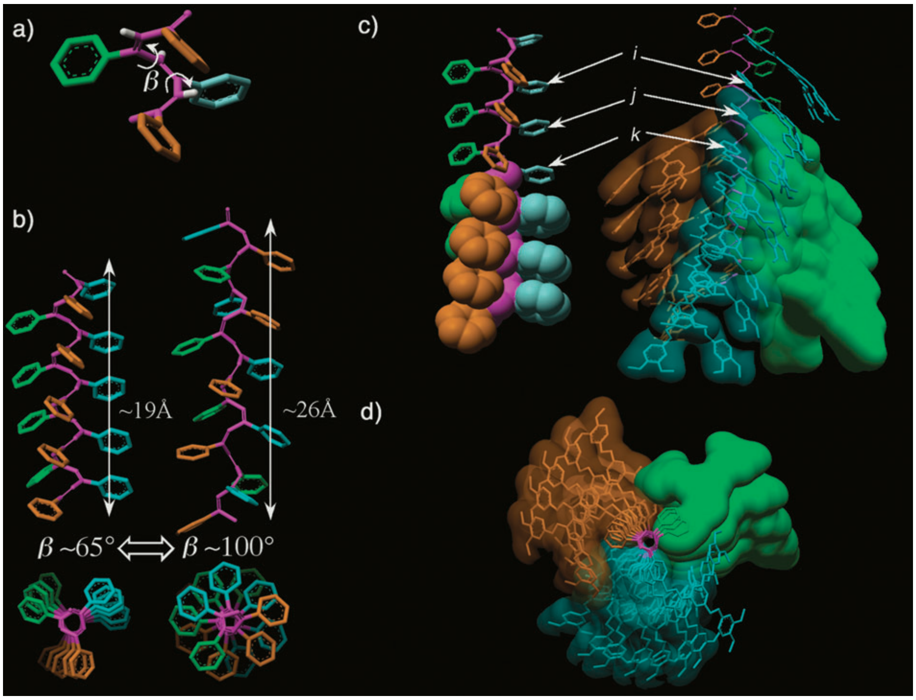


Fig. 2 Model illustrating the (a) dihedral angle (β) about the single bond in the polyene backbone, (b) side and top views of PPA oligomers with $\beta \sim 65^\circ$ (*cis*-cisoidal) and $\sim 100^\circ$ (*cis*-transoidal) and the corresponding change in length along the helix axis, (c) side views of space filling models of PPA and poly[(*3*,*4*-*3*,*5*)*m*G2-4EBn] showing the helical registry of aromatic rings that explains the 6.6 Å feature in the Φ_h^{io} phase, and (d) a top view of a space filling model of poly[(*3*,*4*-*3*,*5*)*m*G2-4EBn] with low electron density core. (Reprinted with permission from ref. 14. Copyright 2005, American Chemical Society.)

unprecedented conformational isomerism that allows their interconversion.[14] Notably, this model suggests that in the Φ_h^{io} phase the polymer is in a *cis*-cisoidal conformation ($\beta < 90^\circ$) while in the Φ_h phase the polyene backbone adopts a *cis*-transoidal conformation ($\beta > 90^\circ$). The values noted in Fig. 2 were chosen to best fit the structural data. An underlying factor may be that contraction of the peripheral alkyl chains causes the dendron to occupy more space along the cylindrical axis.

Given the thermal transformations known to occur in PPA,[40–44] it is necessary to confirm the structural integrity of dendronized PPAs during thermal annealing or cycling. Gel permeation chromatography (GPC) and ^{1}H NMR spectroscopy were used to demonstrate the stability of poly[(*3*,*4*-*3*,*5*)

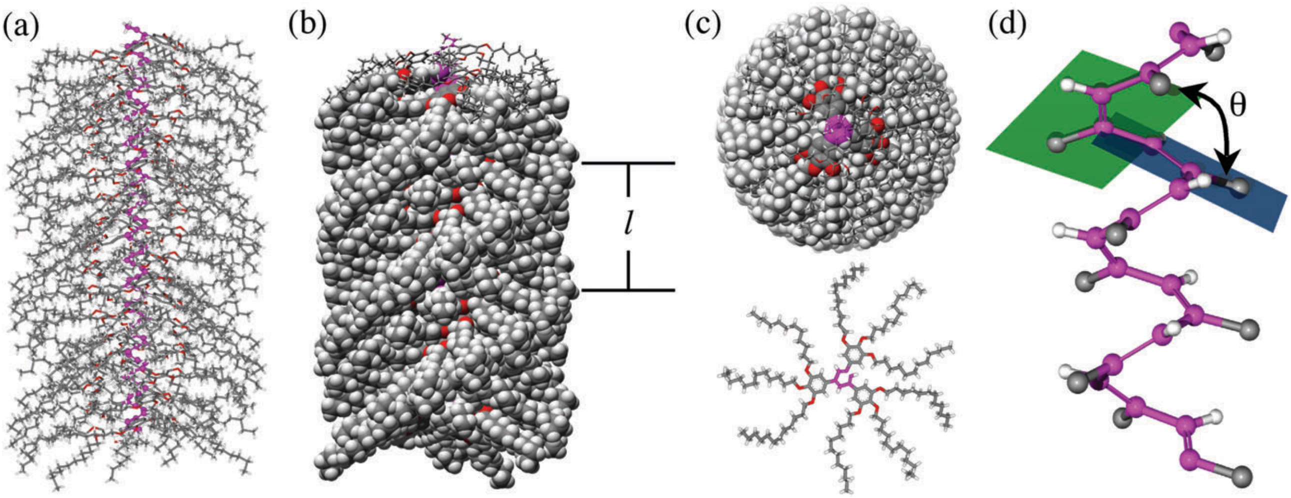


Fig. 3 Structure of the cylindrical macromolecule P[(*3*,*4*,*5*)12G1-A]. Side-view renderings as (a) stick and (b) space filling models, (c) top view of the column and of a column stratum, and (d) detail of the polymer backbone. An increase of the indicated dihedral angle (θ) of approximately 3–5° is enough to modify the average column stratum thickness from 4.1 Å observed in the 3D $\Phi_{r\text{-}c,k}$ phase to 4.4 Å in the 2D Φ_h phase. (Reprinted with permission from ref. 16. Copyright 2006, American Chemical Society.)

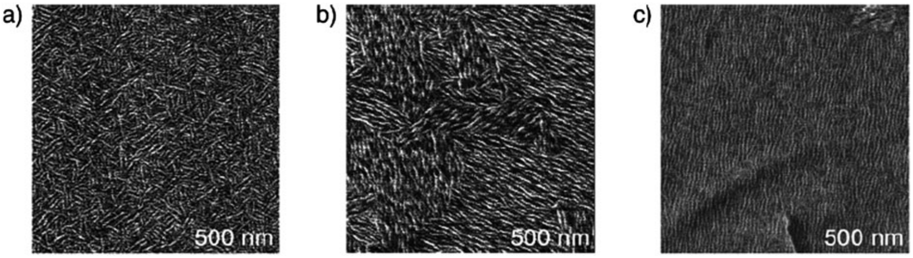


Fig. 4 High-resolution AFM phase image of a single layer of poly[(*3*,*4*-*3*,*5*)12G2-4EBn] (a) spin-cast on HOPG and after annealing for 1 h at (b) 50 °C and (c) at 100 °C. (Reprinted with permission from ref. 17. Copyright 2006, American Chemical Society.

12G2-4EBn] annealed in bulk under argon or ambient atmosphere.[14] This is attributed, at least in part, to inhibition of the cyclization reaction when the polyene backbone is extended in the Φ_h phase. Furthermore, GPC was used to confirm that deleterious thermal transformations do not take place during solution characterization of PPAs dendronized with self-assembling dendrons.[14–16]

Change in the average layer thickness (*l*) due to branching in the peripheral alkyl tails was identified by comparison of P[(*3*,*4*,*5*)12G1-A] and P[Cl-(*3*,*4*,*5*)12G1-A] with P[(*3*,*4*,*5*)dm8G1-A] (Scheme 4).[16] Wide angle XRD patterns from oriented fiber samples can be used to experimentally determine *l*. Fig. 3 illustrates a model for helical intracolumnar order for P[(*3*,*4*,*5*)12G1-A] based on the experimental results from structural and retrostructural analysis.[16] A very small deflection (*e.g.*, 3–5°) of the dihedral angle (θ) can account for the observed ~10% larger *l* for P[(*3*,*4*,*5*)dm8G1-A].[16]

Crystalline order of PPAs dendronized with phenylene ethynylene dendrons has been characterized in bulk to determine the diameter of these polymers.[50–54] Only a first-order reflection is observed. The authors presume pseudohexagonal packing of the dendronized polymer chains in order to calculate molecular dimensions.[50–54] In the examples above second- and third-order reflections are observed. In cases where higher order reflections are absent, the lattice symmetry is assigned by very close structural analogy.[14–16] Similar analogies are not possible for PPAs dendronized with phenylene ethynylene dendrons. Molecular models of the crystalline PPAs dendronized with phenylene ethynylene dendrons overestimate the cylindrical diameter compared to XRD.[50–54] Despite these limitations there is a clear dependence of the observed first-order reflection on the dendron generation and length of the peripheral groups. If this is the macromolecular diameter, then the phenylene ethynylene dendronized PPAs are significantly smaller than the self-assembling dendrons at equivalent generation.

Visualization at interfaces by AFM

Both as individual macromolecules and as ordered arrays, dendronized polymers present a unique opportunity to explore the conformations and self-organization of cylindrical macromolecules.[3,4,8,11,13,15,17] For dendronized polymers whose dimensions are known from some other technique (*e.g.*, XRD in bulk) it is possible to distinguish single macromolecules from aggregates. Furthermore, with potential opportunities envisioned as bottom-up self-assembly in nanotechnology and expression of molecular chirality at interfaces direct visualization becomes increasingly important.

Dendronized polyarylacetylenes have been visualized on both highly ordered pyrolitic graphite (HOPG)[13,15,17] and mica.[15,52] Monolayer films of PPAs dendronized with first- or second-generation phenylene ethylene dendrons were obtained and visualized on mica.[52] No lateral resolution of individual cylindrical structures could be seen in the images, but the height profiles in both cases provided evidence for a single molecule thick adsorbate. The measured heights from AFM are both ~4 Å larger than measured by XRD.[52] A monolayer of poly[(*3*,*4*-*3*,*5*)12G2-4EBn] was visualized on mica.[15] Lateral resolution of cylindrical objects with 2D nematic order was obtained. The average width of the cylindrical objects matched the column diameter from XRD experiments in bulk.[14,15]

Polymers dendronized with self-assembling dendrons exhibit epitaxial adsorption on HOPG due to interaction with the peripheral alkyl tails.[3,4,11,13,15,17] This has also been found for monolayers of dendronized polyarylacetylenes on HOPG.[13,15,17] Annealing studies reveal increased domain sizes that are oriented along a given symmetry axis of the underlying HOPG (Fig. 4).[13,15,17] Remarkably, these relatively short cylindrical macromolecules appear to self-assemble along their cylindrical axis to form very long rod-like structures in bulk.[13,15,17] By contrast, monolayers of a PPA lacking dendrons and exhibiting lyotropic liquid crystalline (*i.e.*, cholesteric) phases exhibit no periodic or helical order.[64]

Epitaxial adsorption of the peripheral alkyl chains results in deformation of the cylindrical macromolecules.[3,4,11,13,15,17] Consequently, the average width of the cylindrical objects is larger than what is found by XRD in bulk.[13,15,17] Nonetheless, correlation of the average width and height of the deformed cylindrical objects can be related to XRD.[17]

In double layers on HOPG the orientational organization due to epitaxial adsorption is only found in the underlayer.[17] The top layer is readily deformed making it difficult to resolve individual cylindrical macromolecules. The height of a double layer of poly[(*3*,*4*-*3*,*5*)12G2-4EBn] was found to be twice that of the monolayer, as expected for well-defined cylindrical macromolecules.[17] Epitaxial adsorption of PPAs lacking dendrons and exhibiting lyotropic liquid crystalline (*i.e.*, cholesteric) phases is believed to disorder the first adsorbed layer.[64] AFM visualization of aggregates comprising the upper layer reveals features related to single-handed helical chirality of the aggregate.[64]

Helical structures found in solution and in bulk suggested the potential to visualize helical chirality in monolayers of dendronized polyarylacetylenes. Nonetheless, it has not, as yet, been possible to identify structural features indicative of the helical conformation in dendronized polymers with achiral peripheral alkyl tails. Visualization of dendronized polymers with chiral, non-racemic alkyl tails have yet to be reported. By contrast, it has been possible to visualize intracolumnar helical features in self-assembled supramolecular dendrimers.[36,65]

Generality of the helical conformation of dendronized polymers

The library of dendronized PPAs[14,15,17] in Scheme 7 was designed to closely match a previously reported library of dendronized polystyrenes (PSs).[4] Strictly speaking the two polymers differ only by the reduced degrees of conformational freedom available to the conjugated polyene backbone. A possible model for the conformation of the PS backbone invoked a helical arrangement, but convincing evidence was provided only for dendronized poly(methacrylate)s with oligo(oxyethylene) spacers.[38]

Structural and retrostructural analysis of the dendronized PPA library[14,15] demonstrate close structural analogy to PS dendronized with self-assembling dendrons.[4] Comparison of the experimental column diameter, layer thickness, density, and number of dendrons per column stratum for dendronized PPAs and PSs confirm the initial design strategy.[14,15] Given that dendronized PPAs have been shown to adopt a helical conformation whose handedness can be selected by peripheral chiral tails,[14,15] we infer a similar conformation for dendronized PSs.

It is not self-evident that this generalization extends beyond those polymers dendronized with self-assembling dendrons. As discussed above, choice of dendron structure can lead to profound alterations of the backbone conformation. Nonetheless, a host of new concepts might be available within self-organizable dendronized polymers by virtue of helical chirality.

Model for transmitting chiral information

Interest to harness helical chirality in supramolecular materials has motivated significant research in polyarylacetylenes,[2,45,48,61] including the work summarized herein. Utilization the dynamic helical conformation of these polymers requires reliable mechanisms by which a single-handed screw sense can be chosen. The detailed structural and retrostructural analyses of dendronized polyarylacetylenes have elucidated means for accomplishing this task.

Investigation of helical dendronized polyarylacetylenes prepared by the so-called macromonomer approach[13,14,16] or the supramolecular attach-to approach[31] in solution indicates that chiral information closest to the polyene backbone has the greatest impact. This has made it challenging to effect helix sense selection from the periphery of increasingly larger dendrons. Correlating bulk structural features with helix sense selection in solution has elucidated some principles for success.

Green *et al.* have developed a quantitative model for understanding helix sense selection in polymers.[60,61] Each chiral, non-racemic repeat unit has a preferred helical handedness. There is an energetic penalty (ΔG_h) for putting a chiral, non-racemic repeat unit into its non-preferred helix.[60,61] As ΔG_h increases there is a greater bias toward the preferred helical screw sense. For an achiral repeat unit there is no preferred helix and no energy penalty associated with being in either helix.

The average column layer thickness (l) for P[(*3*,*4*,*5*)12G1-A] and poly[(*3*,*4*-*3*,*5*)12G2-4EBn] is the same.[14–16] These two achiral polymers should possess similar helical conformations. The increase of l for P[(*3*,*4*,*5*)dm8G1-A] compared to P[(*3*,*4*,*5*)12G1-A] reflects a small distortion of the helical conformation. This is not found for poly[(*3*,*4*-*3*,*5*)dm8G2-4EBn] compared to poly[(*3*,*4*-*3*,*5*)12G2-4EBn]. Given the close structural analogy between the helical conformations of the two chiral, non-racemic polymers, differences in the CD spectra near the absorption of the conjugated backbone are the result of differences in ΔG_h for the two polymers.

Sergeants-and-soldiers experiments with dendronized poly(ethynylcarbazole)s indicate that expression of single-handed helical chirality occurs better in more compressed helical conformations.[13] At the same time, chiral branching in P[(*3*,*4*,*5*)dm8G1-A] forces the helical conformation to stretch compared to P[(*3*,*4*,*5*)12G1-A]. This distortion of the backbone conformation is the direct consequence of the steric interactions between chiral chains. It is straightforward to envision that, for a fixed number of chiral, non-racemic alkyl tails, as the stereocenters are moved farther out radially there are fewer contacts (or collisions) between them. In practice, going from P[(*3*,*4*,*5*)dm8G1-A] to poly[(*4*-*3*,*4*,*5*)AmylG1-4EBn] increases the diameter of the cylindrical macromolecule and no CD signal is observed for the latter polymer.[15,16] Increasing the number of stereocenters per repeat unit by one leads to recovery of helix sense selection in CD spectra of poly[(*3*,*4*-*3*,*5*)dm8G2-4EBn]. Taken together these three observations are related by the density of stereocenters in a cylindrical macromolecule.

The argument for the density of stereocenters causing differences in ΔG_h is different from other means for steric communication of chiral information.[16] Other explanations rely on gear-like interaction between chiral groups[66] or atropisomerism that leads to propeller-like arrangements in a chiral stack.[39] Such events involve relatively specific interactions between chiral groups. The reduced melt temperature and lower enthalpy for the $\Phi_{r\text{-}c,k}$-to-Φ_h transition of P[(*3*,*4*,*5*)dm8G1-A] *versus* P[(*3*,*4*,*5*)12G1-A] suggest that the former is more weakly ordered.[16]

Perspectives

High *cis*-content dendronized polyarylacetylenes are prepared by polymerization of dendritic monomers using Rh-based catalysts[13–17,50–54] or non-covalent association of ionic functionalities.[31] The diameter and internal organization of the resulting dendronized polymers is impacted by the dendron structure (*i.e.*, size, composition, and peripheral functionality).[13–17,31,50–54] Polyarylacetylenes carrying self-assembling dendrons assume cylindrical shapes that self-organize into periodic structures in bulk and at interfaces,[13–17] while other types of dendrons form only crystalline order.[50–54]

Dendronized polyarylacetylenes adopt a helical conformation whose handedness can be selected by peripheral stereocenters[13,14,16] or association of chiral, non-racemic molecules.[31] In bulk, a helical conformation has been found for dendronized PPAs that lack stereocenters. This has only been shown for self-organizable dendronized PPAs,[14–16] but appears general for polymers dendronized with self-assembling dendrons.[15] A mechanism for transmission of chiral information over long distances has been advanced based on the density of stereocenters.[16]

Some unique opportunities have emerged for dendronized polyarylacetylenes. First, porous cylindrical PPAs have been discovered.[14] The porous columns undergo thermoreversible *cis*-cisoidal to *cis*-transoidal conformational isomerism. Concurrent with this transition the pore size contracts below the limit of experimental detection.[14] This process suggests that gating of the pore might be possible.[2] Second, the discontinuous change in column diameter is accompanied by elongation along the cylinder axis.[14] The process is measured on the molecular scale, but it manifests as a bulk material property in oriented fiber samples.[14] Finally, dendronized PPAs have shown promise as permselective membrane materials. This aspect has been recently reviewed elsewhere.[53]

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