

Molecular Modeling Simulations of the Morphology of Polyphenylene Dendrimers

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Three polyphenylene dendrimers were studied by molecular modeling techniques with the goal of better defining the notion of shape persistence often associated with these molecules. We show that despite the rigidity of the monomers, a large variety of dendrimer morphologies is accessible, in large part due to the asymmetrical branching pattern of the monomers (they have nodes in meta and para positions with respect to their anchor point). The folding ability of a branch depends on the number and sequence of the meta and para nodes it contains: while some of the branches are always straight, others can fold back, and the amplitude of that folding increases with generation. As a result, the range of accessible morphologies increases with the generation, from a dense-shell model in low generation to a model intermediate between a dense shell and a dense core in high generation. When the typical A₂B monomer is replaced by an A₄B monomer, the dense packing limit is reached as early as the second generation because of a higher density and the presence of nodes in the ortho position, which are oriented backward.

Introduction

Dendrimers are well-defined highly branched macromolecules composed of three distinctive regions: an initiator core, branching units radiating from the core, and endgroups. Dendrimers are usually drawn with a highly symmetrical shape corresponding to a dense-shell model: the branches are shown extended, empty cavities are seen close to the core, and the branch density increases outward. However, most dendrimers (e.g., poly(propylene imine) systems) are actually formed of flexible branches that can fold back, fill the inner cavities, and disperse the endgroups throughout the molecular volume.^{1–5} Such structures correspond to a dense-core model, for which the branch density is at a maximum at the center of the molecule and decreases outward. As many potential applications of dendrimers were inspired by the dense-shell picture of the molecule (i.e., based on exploiting a molecular surface covered with the many functional endgroups and free cavities within the structure), much research was—and still is—devoted to finding ways to control the location of the endgroups. One solution consists of building dendrimers with rigid branches that do not fold back.

The latter strategy was followed by Müllen and co-workers who assembled stiff building blocks, benzene rings, to obtain a rigid dendrimer scaffold.^{6–11} They used a well-established synthetic method for the construction of polyaryl compounds based on a Diels–Alder reaction of tetraphenylcyclopentadienone derivatives with alkynes. The Diels–Alder reaction results, after elimination of CO, in the addition of structural units comprising five benzene rings (these structural units are referred to as monomers in this paper; see Figure 1). Used in cascade, the procedure rapidly leads to polyphenylene dendrimers of a large molecular weight. Exploiting the numerous

possibilities that a rigid scaffold affords (small changes in the design parameters of the dendrimer can translate into large morphology changes), Müllen's group fine-tuned the dendrimer properties by modifying the nature and geometry of the core, the number of branches, the branching pattern of the monomers, and the nature of the endgroups.^{6,7} Studies of these molecules address potential applications as diverse as catalyst carriers,¹² emissive nanoparticles,¹³ light-harvesting systems,^{14,15} substrates for biological applications,¹⁶ chemical vapor sensors,¹⁷ templates for metal nanoparticles,¹⁸ and precursors of polycyclic aromatic hydrocarbons.^{8,11} The dendrimers also can be used as building blocks to dendronize polymers and confer them new properties¹⁹ or to construct even more complex supramolecular structures such as nanocomposites^{18,20} and nanofibers.^{21,22}

At first, the notion of shape persistence associated with the polyphenylene dendrimers was largely qualitative since it was based mainly on assumptions—other polyphenylene systems are seen as rigid—or indirect evidence—some experimental results could only be explained by some sort of rigidity effects of the dendrimer scaffold. Later, various studies (molecular dynamics,²³ solid-state NMR,²⁴ neutron diffraction,²⁵ and AFM^{26,27}) provided more quantitative evaluations of the rigidity and shape of the molecule. However, the degree of shape persistence of the polyphenylene dendrimers is still imperfectly known and appears more complicated to define than initially thought, for two structural parameters counter the rigidity effect of the building blocks: the inter-ring connection, a single bond around which rotations allow the monomers to have different orientations, and the branching pattern that is asymmetrical. In particular, the interpretation of the neutron diffraction experiments performed by Rosenfeldt et al.,²⁵ which were key in assessing the static properties of polyphenylene dendrimers, has completely neglected to consider the role of the branching pattern asymmetry: the coarse-grain model of the dendrimer used to interpret the scattering data was indeed given a symmetrical branching pattern. This study concluded that the

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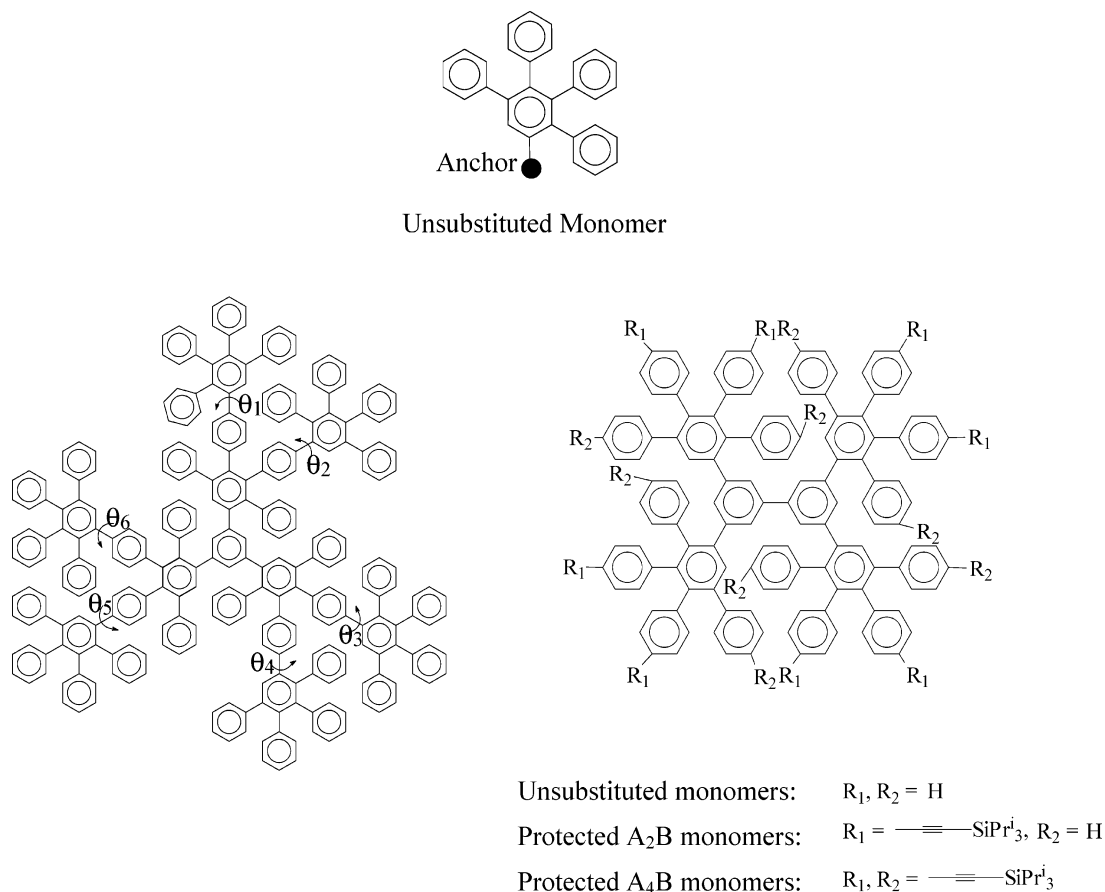


Figure 1. (Top) Unsubstituted monomer. (Left) G2 dendrimer built on a three-fold core. Torsion angles responsible for the changes in monomer orientations in the second layer are labeled. (Right) G1 dendrimer built on a biphenyl core. Position of the reactive endgroups necessary to build G2 is indicated for both A_2B and A_4B protected monomers.

monomers of the different layers are well-separated from each other (i.e., that backfolding does not occur). However, that this conclusion remains valid when the correct, asymmetrical branching pattern is used has to be assessed. The study also revealed that the interactions among the dendrimers in toluene are soft (i.e., there is no well-defined distance beyond which the strength of repulsion diverges), suggesting that two molecules can overlap. Such a behavior has been reported for flexible dendrimers,²⁸ which are known for having a density decreasing toward the periphery—they conform to the dense core model—thus allowing entanglement between branches of neighboring molecules. Thus, can we reconcile a behavior typical of dense-core molecules with the dense-shell model (where monomers are congested in the periphery) thought to correspond to polyphenylene dendrimers?

In the present work, three polyphenylene dendrimers were modeled with molecular mechanics to better understand how the morphology of the dendrimer is shaped by the following parameters: the asymmetrical branching patterns, rotations around the inter-ring bonds, core geometry, number of branches, and generation.

Systems under Study

We first consider a polyphenylene dendrimer built on a three-fold core (see Figure 1, left). The monomers are of the A_2B type (i.e., with two reactive endgroups per monomer). This results in the doubling of the number of peripheral monomers at each generation. Stable morphologies of the first six generations (G1–6) were obtained via a conformational search. The simulations were performed on isolated molecules to focus on

the intrinsic factors affecting the morphology. When no solvent molecules or solvent effect corrections are taken into account, the simulations tend to stabilize the compact conformers most strongly. The conformational search was thus driven in conformity with this tendency (i.e., toward compact and organized morphologies showing an optimal packing of the monomers within the branches). Such morphologies are to be present in a bad solvent. A dense packing of the monomers is also expected for dendrimers in the solid state, although the global shape of the molecule is likely to be different due to the influence of intermolecular interactions. The compact morphologies studied here are thus appropriate to provide insights into how intramolecular interactions are optimized in the presence of structural constraints. As these morphologies are highly ordered, they also allow us to spot easily a generational transition in the dendrimer morphology. At the other end of the organization scale lie open morphologies with loosely packed branches. Although such morphologies are less stable in our simulation conditions, they can become stabilized in an appropriate environment, such as in a good solvent. These open conformers are discussed and compared to the compact conformers.

The second and third systems studied in this work are polyphenylene dendrimers built on a biphenyl core. They differ by the branching pattern of the monomers: A_2B and A_4B (Figure 1, right). Although A_2B monomers are most commonly used to build polyphenylene dendrimers, A_4B monomers have also been used.^{7,10} The latter monomers allow a much faster growth of the dendrimer than the former (due to a four-fold increase in the number of peripheral monomers at each generation instead of a doubling). Actually, the growth is so

fast that steric limitations appear as soon as in the second generation. The first generation is built by reacting a biphenyl bearing four ethynyl groups with cyclopentadienones. When the cyclopentadienones are terminated by silyl protected ethynyl functionalities, the growth of the dendrimer can be carried on beyond the first generation. The ethynyl groups are deprotected, then submitted to a new round of reactions with cyclopentadienones, which leads to the grafting of a new layer of monomers. When using A₄B cyclopentadienones bearing silyl protected ethynyl functionalities, the first generation is easily synthesized, but in the second generation, a mixture of products is obtained, namely, the targeted sixteen-fold product and mainly a fourteen-fold product. The preferential formation of the fourteen-fold product was attributed to a sterically induced stoichiometry. When building G₂ with the less bulky unsubstituted cyclopentadienones, the expected sixteen-fold product is obtained. These results tend to indicate that G₂ built with A₄B monomers is at the dense packing limit, which is characterized by a surface so tightly congested that the growth of the dendrimer is precluded. The two dendrimers studied here thus allow evaluating the influence of the branching pattern on the morphology and appearance of the dense packing limit. The conformational search was focused on compact morphologies (with the remarks made for the system built on a three-fold core valid as well).

Methodology

General Procedure. The molecular simulations were carried out using the Cerius² molecular modeling package from Accelrys Software Inc.²⁹

The potential energy surface of the systems was reproduced by the UFF force field^{30–32} and explored using a systematic method called a grid scan procedure: some specified torsion angles were varied over a grid of equally spaced values, and each conformation generated by that procedure was optimized by molecular mechanics. As the method quickly becomes burdensome with the number of torsions to vary, the choice of the torsions and of their variational increments is critical. To limit drastically the number of conformations generated while exploring the conformational space as extensively as possible, different rules were applied.

(i) The generations were built following a stepwise procedure. For low generations, each growth step was achieved by grafting a new layer of monomers on one of the most stable conformers of the previous generation. Only the torsions changing the orientation of the monomers of the new layer were varied. This divergent procedure proceeded up to G₄ (up to G₂ with A₄B monomers). From G₅ on, overcrowding appears in the added layer. Relieving the congestion necessitates changes of monomer orientation within the inner layers. Since adding these changes in the frame of a divergent procedure would have increased excessively the simulation time, the building procedure was modified from divergent to convergent. To build G₅, dendrons of an optimized G₄ conformer were grafted to an optimized G₁ conformer (two dendrons per monomer of G₁). The orientation of the dendrons was then varied by means of the grid scan procedure. For the dendrimers built on a three-fold core, the method has been extended to G₆, by grafting six dendrons of G₅ to G₁.

(ii) The peripheral phenyls of the added monomers were set orthogonal to the central aromatic ring. This structure, which corresponds to a transition state in an isolated monomer, allows the phenyls to tilt easily in any preferential direction during the geometry optimization.

(iii) As two monomers grafted on the same monomer generally tilt in the same direction, the torsion increments given

to those two monomers were determined to avoid redundant conformations. The torsion of the first monomer was varied from -135 to 135° by steps of 90° , allowing it to cross the four valleys of potential energy found by a 360° rotation of the monomer. The torsion of the second monomer was set to 180 and 0° . These values correspond to transition states for an isolated monomer and allow the second monomer to tilt easily in either of the two closest minima imposed by the first monomer.

(iv) Some monomers were so tightly packed that the values given to the torsions had to be modified to prevent entanglement.

(v) When the dendrons grafted on the core did not interact with each other, the dendrons were cut off from the core and separately submitted to the conformational search. The most stable dendrons were then grafted back to the core, and the whole dendrimer was then submitted to a further geometry optimization.

Energy Minimization by Molecular Mechanics. The energy minimizations were performed with a conjugate gradient algorithm using a convergence criterion of 0.001 kcal/mol Å. The long-range interactions were smoothly turned off between 11 and 14 Å using a spline switching function. The electrostatic interactions were taken into account by way of point charges determined by the Qeq charge equilibration algorithm³³ and located on the nuclei. As the charge assignment depends on the geometry, the charges had to be recalculated regularly during the geometry-optimization process—here every 500 minimization steps—until consistency between the charges and the geometry was reached.

Dendrimers Built on a Three-Fold Core with A₂B Monomers

Role of the Branching Pattern. The monomers have an asymmetrical branching pattern: the branching nodes are para and meta to the anchor point of the monomer (see Figure 2, top). For years, asymmetrical building blocks have been known to provide the dendrimers with properties that vary from one branch to the next—one of the first dendrimers synthesized was the polylysine-based dendrimer of Denkewalker et al., which has branches of different lengths due to asymmetrical building blocks.³⁴ In the polyphenylene dendrimers, the asymmetry does not affect the length of the branches but modifies their folding properties, depending on the number and relative proportions of the para and meta nodes they contain, as well as the sequence of the nodes along the branches. Within a dendron, all combinations of para and meta nodes occur, with only one all-para branch (i.e., with all the monomers in para orientation) and one all-meta branch.

Branching in para amounts to growing a branch linearly. The all-para branch is thus made of aligned phenylenes from the core to the periphery. Branching in meta amounts to growing a branch laterally, at an angle of 60° with respect to the previous growth direction. The all-meta branch is thus made of a succession of monomers at an angle of 60° with respect to their bonded neighbors, from the core to the periphery. This configuration allows the all-meta branch to orient backward, with an amplitude of folding that increases stepwise with the number of monomers (i.e., with generation). A simple way to obtain a good idea of the maximum folding amplitude as a function of generation is to follow the edges of a hexagon, each edge representing the orientation of one monomer. Significant back-folding for the all-meta branch is thus possible for G₄ on (see the schematic all-meta branch folded to its maximum in Figure 2, bottom right).

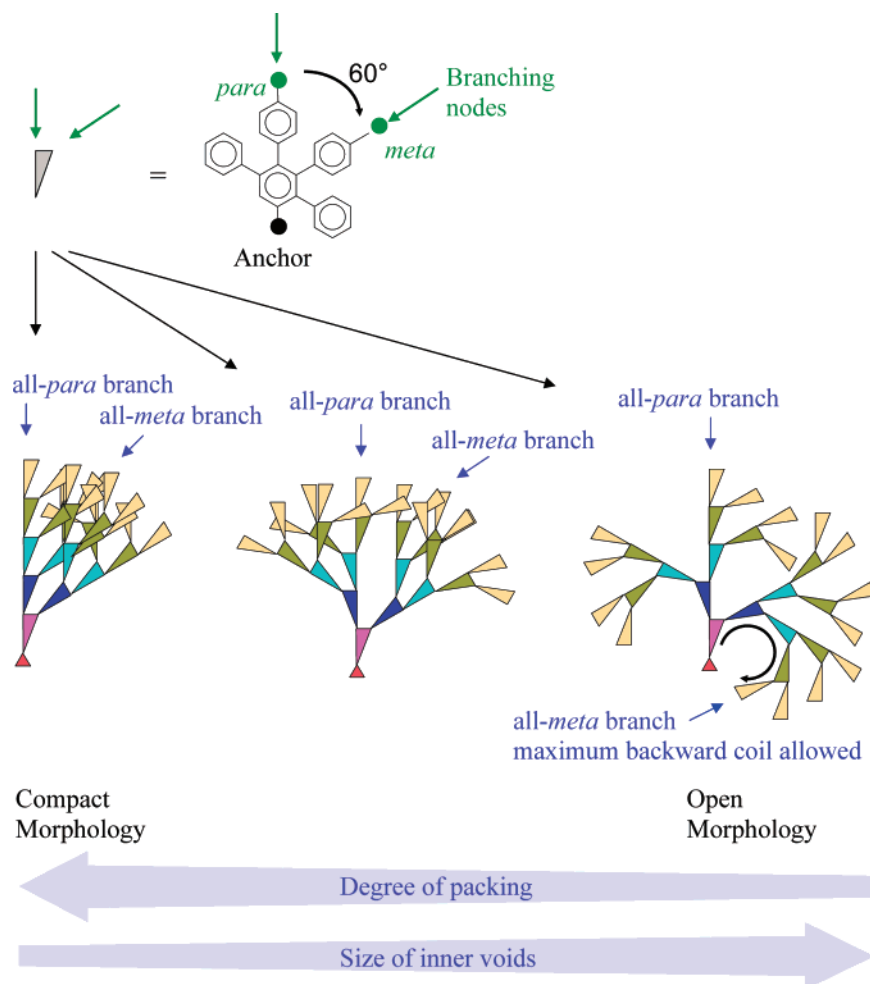


Figure 2. (Top) A_2B monomer with its branching nodes in para and meta positions with respect to the anchor point and its schematic representation. (Bottom) Conformers of a G_5 dendron made out of such schematic A_2B monomers. The conformers were obtained by changing the orientation of the branches via rotations around the inter-ring single bonds. The branch with all the monomers grafted in para positions (i.e., aligned) is referred to as the all-para branch; the branch with all the monomers grafted in meta positions (i.e., at an angle of 60° relative to their bonded neighbors) is referred to as the all-meta branch.

Despite the rigidity of the monomers, the branches can thus partially fold back in the polyphenylene dendrimers, with a maximum amplitude that differs from one branch to the next. The all-para branch is always straight and extended, while the all-meta branch can be either extended or folded, depending on the inter-ring rotations between the monomers. The other branches behave between these extremes as they are based on a combination of monomers grafted in meta and para positions.

Role of Inter-ring Rotations. A full rotation of a monomer leads to four energy minima that differ by the orientation of the branches borne by the rotating monomer, as in the course of the rotation the branches are rigidly dragged off due to their stiffness. But, the amplitude of the displacements depends on the orientation of the branches relative to the rotation axis, which is oriented along the bond in para orientation: large displacements for branches that make an angle with the rotation axis (i.e., a monomer grafted in the meta position) and small displacements for branches in the prolongation of the rotation axis (i.e., a monomer grafted in a para position). In an all-para branch, the rotation axes of the monomers are all aligned. As a result, the conformational changes are minimal; the all-para branch forms the only part of the molecule that can be considered really invariant, whatever the conformation, and determines the dimensions of the molecule (see Table 1). In the all-meta branch, the rotation axes of the monomers are not

TABLE 1: Dimensions of Six Generations of Polyphenylene Dendrimers Built on a Three-Fold Core^a

	G1	G2	G3	G4	G5	G6
L (Å)	10.0	18.6	27.3	35.9	44.5	53.1
D (Å)	17.4	32.3	47.2	62.1	77.1	92.0

^a Length (L) of the straight all-para branches determined from the center of the core, and distance (D) between the endgroups of any two straight all-para branches.

aligned, which explains why the conformations of an all-meta branch can have quite different shapes, from folded to extended.

The rotation of the monomers around the single inter-ring bonds thus plays a critical role in giving the conformational freedom necessary for the molecule to adapt its shape to the environment or to the steric constraints imposed by its size. As schematically depicted in Figure 2, selected rotations within a dendron can make the shape evolve from highly compact and conic to open and curled back to a certain extent. More evidence of that behavior is given by the pictures of two G_5 conformers

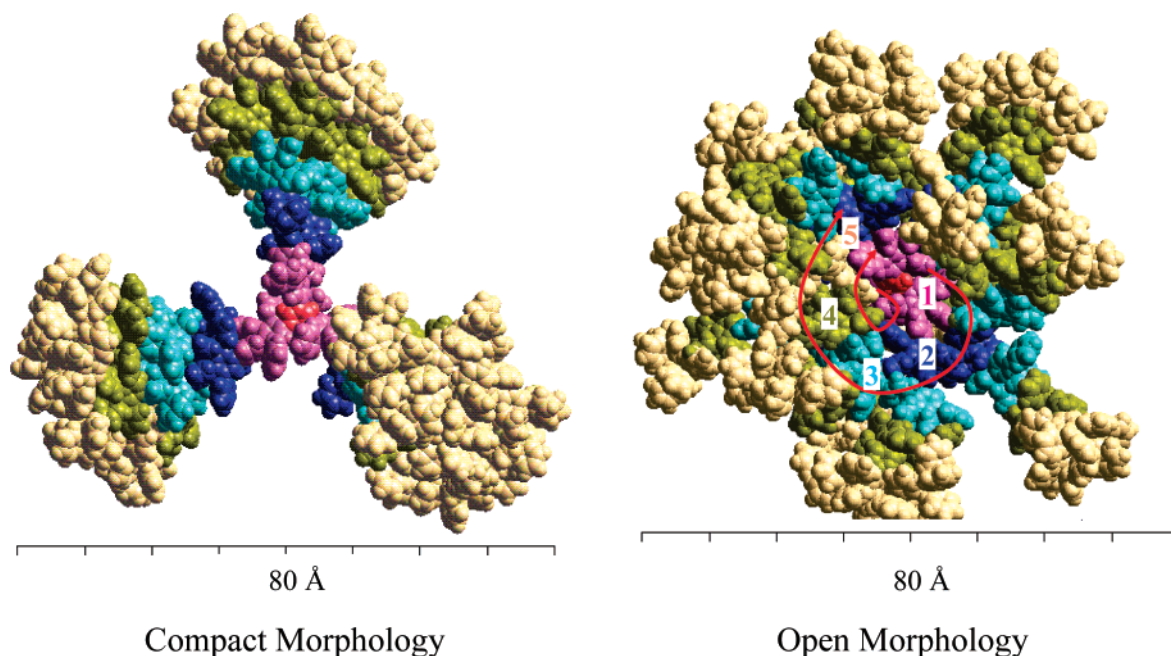


Figure 3. Compact (left) and open (right) conformers of a G5 dendrimer built on a three-fold core. For the open morphology, two arrows highlight a branch that folds back down to the core; its monomers are labeled as a function of the layer to which they belong. Core is displayed in red; the colors of the monomers are made to evolve with the layers as follows: purple, blue, turquoise, light green, and yellow.

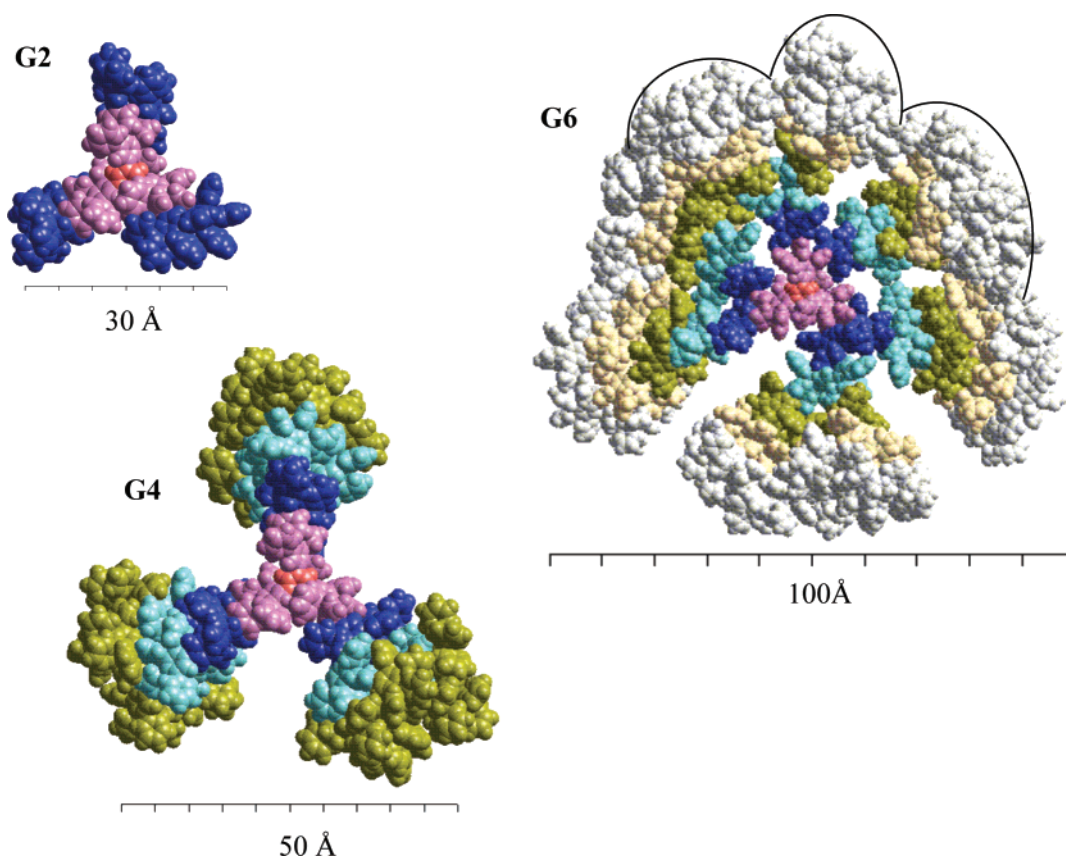


Figure 4. Compact conformers of G2, G4, and G6 dendrimers built on a three-fold core. For G6, the curvature of the top layer of one dendron split up into three smaller dendrons is highlighted.

(Figure 3), one with compact dendrons (referred to as a compact conformer) and one with open dendrons (referred to as an open conformer). In the picture of the open conformer, two arrows delineate the monomers belonging to an all-meta branch that folds back down to the core.

Generational Evolution of the Branch Packing. For the compact conformers of low generation dendrimers, the three

dendrons shape into compact cones. The monomers added at each growth step aggregate tightly into layers that are well-segregated, one monomer thick, and whose extension doubles at each generation (see G2 and G4 in Figure 4). A doubling of the layer surface at each generation can occur without disrupting the monomer packing within the inner layers for the first generations only due to the very structure of the dendrimer and

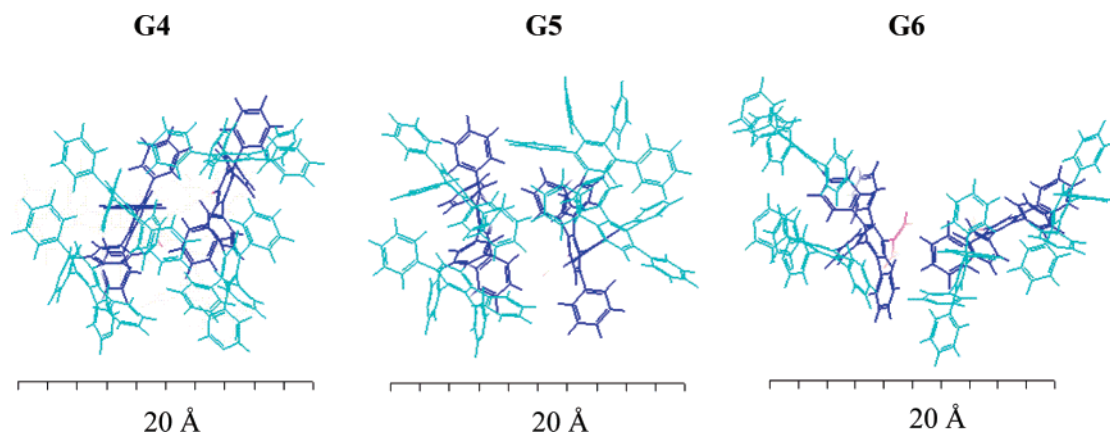


Figure 5. Organization of the monomers in the second and third layers of a dendron, from G4 to G6 dendrimers built on a three-fold core.

the limited mobility of the monomers. From G5 on, the conic morphologies open at the level of the inner layers to avoid overcrowding in the outer layers (see Figure 5). This goes together with a bending of both the inner and the upper layers. Eventually, with further growth of the dendrimer, the whole dendrons split up into smaller dendrons, which are partly separated; they are separated by channels at the level of the inner layers while still being in close contact in the periphery (see G6 in Figure 4). The top layers thus become irregular, being composed of aggregated bended pieces reflecting the effects of the splitting of the main dendrons into smaller dendrons. Separation occurs not only within the main dendrons, but it also occurs between them, but following an opposite generational sequence. Up to the fifth generation, the three main dendrons are well-separated as they radiate from the core in directions at 120° with respect to each other. From G6 on, however, the outer layers of the three dendrons are large enough to meet each other (see Figure 4).

In the compact conformers, the global bending of any layer is rather small in comparison to the maximum degree of folding allowed for some of the branches (in G5 and G6, the all-meta branches could bring the termini close to the core). The absence of folding and marked segregation of the layers were confirmed by the generational evolution of the radial density profiles of the carbon atoms of the different layers as a function of the distance from the core (see Figure 6): the density profiles of the different layers are narrow and show small overlaps and almost no changes upon increased generation. The global density profiles correspond quite well to the density profile of an ideal model of an extended polyphenylene dendrimer, where the volume available to the monomers of each layer grows as concentric shells of thicknesses equal to one monomer length (Figure 6, inset). The density is highest in the first shell next to the core, then decreases in the second and third shells, before rising slowly in each additional shell. The highest generation we studied has six shells (G6), and the density in the last shell is still much smaller than that in the first shell. As the packing in the first shell is far from being optimal, the dendrimer is thus penetrated by voids from the core to the periphery up to high generations, although locally the monomers are strongly packed. There is no dense core sheltered from the environment; the surface region (i.e., the part of the molecule that can be in contact with the environment) extends down to the center of the molecule.

Contrary to compact conformers, open conformers have some degree of backfolding. To evaluate it, the density profiles of both classes of conformers have been compared to one another, as well as to that of a model of a flexible polyphenylene

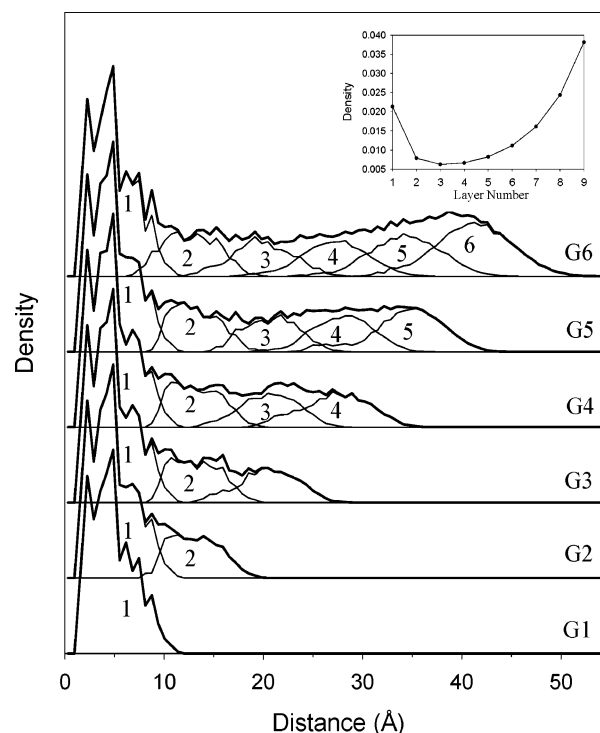


Figure 6. Density profiles of the monomer layers in compact conformers from G1 to G6 dendrimers built on a three-fold core. Total density is represented as dark lines. Inset shows the density within the shells of an ideal model of an extended polyphenylene dendrimer built on a three-fold core in which the monomers of each layer are located in concentric shells of thickness equal to one monomer length.

dendrimer. In that model, the bonds between the monomers and between the three monomers of the first layer and the core were removed to allow a collapse and densification of the morphology upon energy minimization, a behavior characteristic of many flexible dendrimers in bad solvent conditions. The density profiles are displayed in Figure 7 for G5, a generation sufficiently high to observe backfolding (as mentioned earlier, significant backfolding is expected from G4 on). For open conformers, the density profiles of the layers widen when going outward; the higher the layer, the wider its density profile. The density profiles are similar to those of a compact conformer for the first two layers, but they differ for higher layers as their density profiles extend further toward the core, leading to significant overlap between the layers; the monomers of the last layer are found from the periphery to the core. These results are characteristic of backfolding. Backfolding, however, is only partial. The density in the inner part of the molecule is much

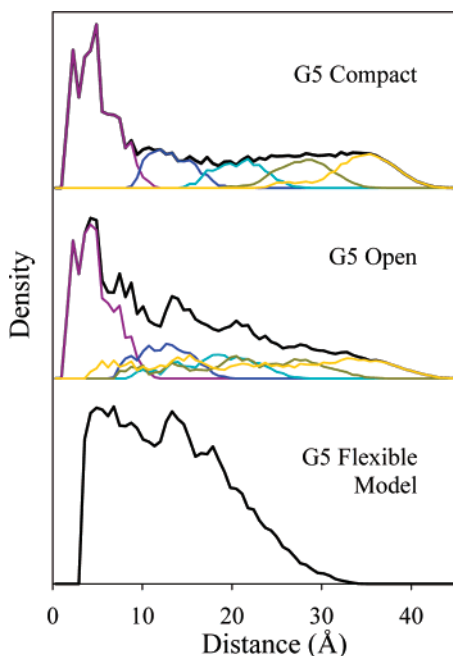


Figure 7. Total density profiles (black lines) and density profiles of the monomer layers (in color) for compact, open, and flexible conformers of a G5 dendrimer built on a three-fold core. Compact and open conformers correspond to those displayed in Figure 3, and flexible conformer corresponds to a model where the bonds between the monomers and between the three monomers of the first layer and the core were removed to favor a dense-core morphology typical of many flexible dendrimers.

lower in the open conformer than it is in the flexible model of the polyphenylene dendrimer. In addition, the density drops to zero much farther from the core (by ~ 10 Å) (i.e., at the same distance as in the compact conformer due to the contribution of the all-para branches, which are unable to fold). Thus, the open conformers are only partially folded and filled and still have many cavities down to the core.

Dendrimers Built on Biphenyl with A₂B and A₄B Monomers

Some compact morphologies of dendrimers built with A₂B monomers (G2–8 and G4–32, with n in G x – n indicating the number of peripheral unsubstituted monomers and x the generation) and A₄B monomers (G2–16) are displayed in Figure 8; the hydrogen atoms corresponding to A in A₂B and A₄B are green, and the core is red. For each of the three systems, two conformers with extreme orientations of the dendrons are displayed. For the sake of comparisons, the cores of the conformers have been oriented in the same way.

Dendrimers made of A₂B monomers were built up to the fifth generation with no overcrowding and with large changes in the orientation of the dendrons allowed. This is illustrated in Figure 8. All the conformers shown have the dendrons aggregated pairwise. But, the pairing occurs between dendrons that are grafted either on the same ring of the core (conformers displayed on the left) or on both rings of the core (conformers displayed on the right). The endgroups are oriented outward and concentrated in small local parts of the molecular surface; the core is largely accessible.

Using A₄B monomers, we were unable to obtain stable conformers beyond the second generation, thus confirming that the dense packing limit is reached early for that system. In addition, in G2, only a few conformers were obtained in the conformational search, and their morphologies are similar (the

dendrons aggregate into a thick belt imperfectly surrounding the core), which means that the conformational freedom is low. This characteristic was also deduced by monitoring the values of the torsion of the biphenyl core. In G2 built with A₂B monomers, the steric strains appear to be moderate, as the torsion of the core ranges between 36 and 46° (i.e., a range found for unconstrained systems such as G1 and isolated biphenyl (42° with the UFF force field)). In G2 built with A₄B monomers, on the contrary, the torsion of the core spans a wider range of values, between 45 and 87° (90° corresponds to the top of the torsion barrier for biphenyl), which reflects an increase of the steric strains and thus a smaller conformational freedom. The tilt of the monomers follows a similar trend, although attenuated (from a 53–83° range in G2–8, i.e., what is also found in G1, to a wider 45–86° range in G2–16). The origin of the steric strains lies in the strong changes that occur in the orientation of the monomers and the density of the molecule when changing the branching pattern from A₂B to A₄B. These effects are clearly seen in Figure 9, where the density profiles of the backbone atoms is shown as a function of the distance from the configurational center for a G2–8 and G2–16 conformer. Both dendrimers have a density dropping to zero at the same distance from the core. Thus, they have the same available volume but are filled by a different number of monomers: G2–16 is much denser than G2–8, and this density increase is observed at any distance from the core (after the 3.5 Å threshold, which marks the smallest distance between nonbonded carbons). The density profiles of the first two layers overlap only slightly in G2–8, indicative of a good segregation between the layers, while they strongly overlap in G2–16, indicative of a mixing between the monomers of the two layers. For both systems, the density profiles of the first layer are similar—they drop to zero at the same distance from the core. The overlap in G2–16 is thus due to monomers of the second layer that come as close to the core as the monomers of the first layer. This behavior cannot be explained by a backfolding promoted by rotations around the single bonds that link the monomers (this effect becomes significant only from G4 on). Instead, it comes from the presence of an ortho junction in the A₄B monomers, forcing a backward orientation of one-fourth of the monomers from the second layer (they form an angle of 120° with respect to the direction of the all-para branch).

Discussion

This study indicates that some of the branches of high-generation dendrimers are able to fold back. This result was unexpected when considering the prevailing description of these molecules found in the literature. However, it must be borne in mind that direct experimental proof dealing with the backfolding issue in polyphenylene dendrimers essentially comes from one single study,²⁵ which unfortunately has not taken into account the asymmetry of the branching pattern. In that study, Rosenfeldt et al. used a coarse-grain model of the dendrimer with a symmetrical branching pattern to interpret the neutron diffraction results. A number of 500 conformers was generated by randomly changing the angles between the units and excluding the conformers when the units overlap. The large number of generated conformers ensures that the most extreme morphologies have been obtained. These data can be compared to the ensemble of open and compact conformers we have obtained, as these conformers also correspond to extreme morphologies. The results given by our model and the Rosenfeldt model are similar in the low generations (the layers of monomers are well-segregated; no backfolding occurs). In high generations, on the

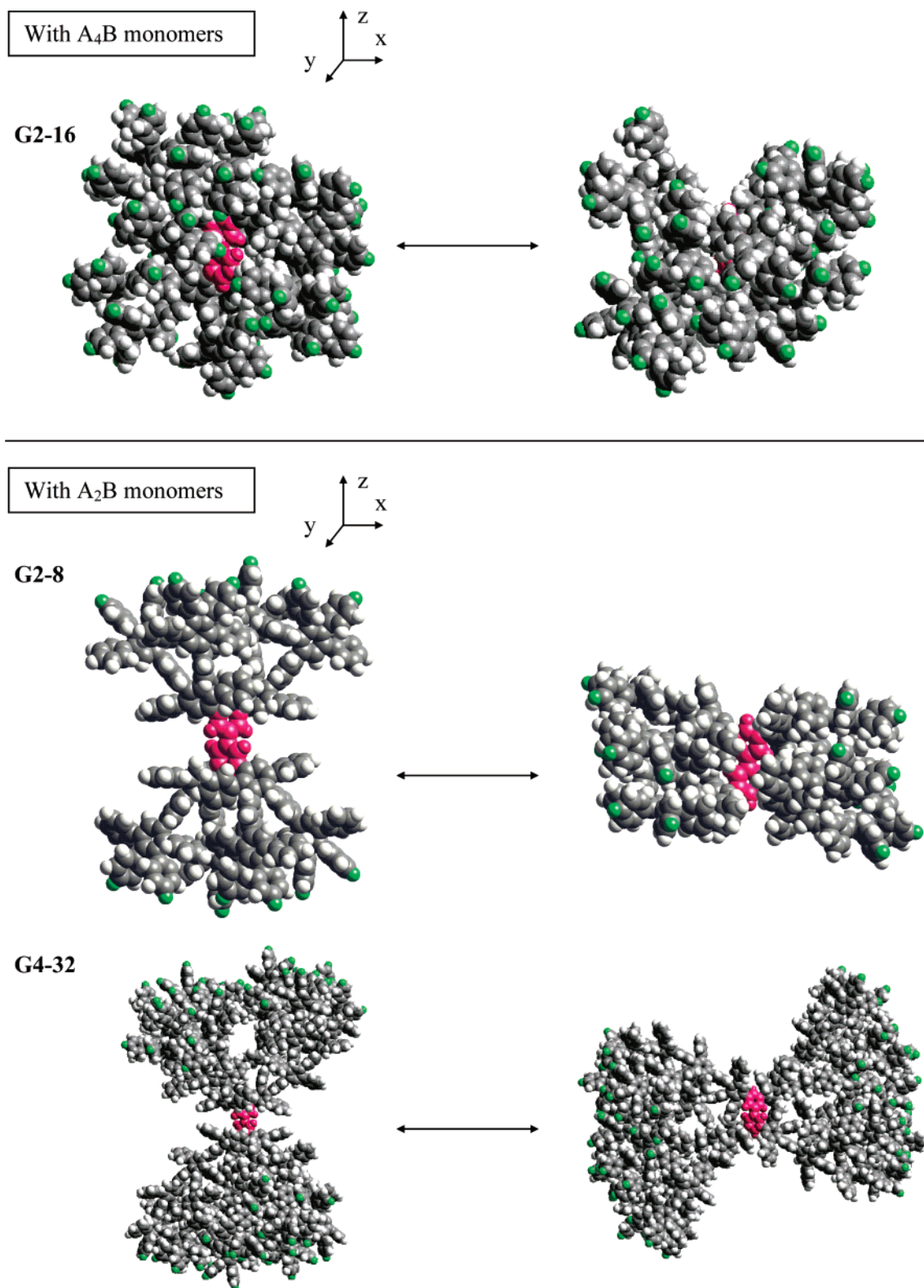


Figure 8. Conformers of dendrimers built on a biphenyl core with A_2B and A_4B monomers. Core is red and endgroups are in green.

contrary, the results diverge. For both models, the layers are spread out over a wider distance, but the amplitude of that spreading is different. The layers are still well-segregated for the model with a symmetrical branching pattern, while they mix for the model with an asymmetrical branching pattern. Clearly, the role of the asymmetry of the branching pattern in the conformational versatility of the branches is present and increases with generation; it matters significantly from G4 on.

Up to now, the dendrimers reported in the literature do not go beyond G4. It is thus when backfolding takes off that the growth of the dendrimer is stopped. The dendrimers built on a biphenyl core with A_2B and A_4B monomers can be synthesized as monodisperse compounds up to the fourth and second generations, respectively. Beyond these respective generations, purity is lost, supposedly due to steric crowding.⁷ For both compounds, synthesis limitations occurred when attempting to

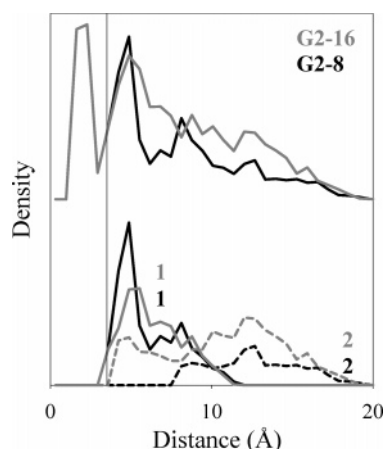


Figure 9. Total density profiles (top) and density profiles of the monomer layers (bottom) of G2 dendrimers built on a biphenyl core with A₂B (G2–8) and A₄B (G2–16) monomers.

graft monomers bearing silyl protected ethynyl functionalities. With A₄B monomers, an incomplete grafting occurred, indicating that the dense packing limit was reached. This behavior was detected by our simulations. Oppositely, with A₂B monomers, the growth of the molecule proceeds beyond G₄, uncontrolled, due to an in situ deprotection of the ethynyl functionalities followed by further addition of monomers. Our simulations, indeed, did not show any steric reason precluding the growth of these dendrimers beyond G₄. The highest generations modeled are G₅ (biphenyl core) and G₆ (three-fold core), and they still have voids in the periphery. From the simulations, two hypotheses can be proposed to explain the different experimental behavior of both types of dendrimers: (i) dendrimers with A₄B monomers have a low conformational freedom. Some of the endgroups are inaccessible for grafting due to their backward orientation, the limited mobility of the monomers that bear them, and the high density of the dendrimer. Comparatively, the dendrimers with A₂B monomers have very different conformers. The branches can direct the endgroups outward where grafting is easy, then fold and trap the grafted monomers in a crowded environment that promotes deprotection. (ii) Another possibility to explain the behavior of the dendrimer with A₂B monomers is that the monomers graft on a compact conformer, which leads to local steric strains that promote deprotection before a reorganization of the branches has time to occur. Indeed, for the compact conformers, G₄ is a limit beyond which a reorganization of the branches must occur.

In both hypotheses, the kinetics of the conformational changes and the height of the torsion energy barriers that drives it likely play a critical role by maintaining the decorated monomers in a crowded environment for a time long enough to promote deprotection.

The range of orientations accessible for the branches, and the presence of large voids allowing the conformational changes, can also explain several experimental observations. For instance, the neutron diffraction studies of Rosenfeldt et al.²⁵ have concluded the interpenetration of the dendrimers in toluene. This result is consistent with our simulation results, which underline that voids extend from the periphery to the core and are wide enough to allow the molecules to intercalate with each other. This could also explain the large variety of morphologies for dendrimer aggregates. When a solution of a dendrimer built on the biphenyl core is cast on HOPG, up to three self-assembled dendrimer morphologies were observed on the same sample: globular aggregates, monolayers, and nanofibers,²² which suggests that the arms of the molecules overlap differently. Thus,

we believe that the properties of the open and compact morphologies can be sufficiently different to confer the polyphenylene dendrimers with significant versatility of shape as a function of the environment (solvent, solid state).

Conclusion

We studied the morphology of polyphenylene dendrimers built from the typical A₂B monomers by molecular mechanics. Despite the rigidity of the monomers, a large variety of dendrimer morphologies is accessible, in large part due to the asymmetrical branching pattern. The grafting nodes in meta and para orientation with respect to the anchor point of the monomers confer the branches with a folding ability that depends on the length of the branch (i.e., the generation) and the sequence and proportions of the para and meta nodes they contain. Within a dendron, all combinations of para and meta nodes occur, with only one all-para branch (i.e., with all the monomers in the para position) and one all-meta branch. The all-para branches are straight and unable to fold back. They define the element of the scaffold that is shape persistent and the extension of the molecule, two properties that are identical in all conformers. The all-meta branches are tortuous and can either extend or fold back. They define the maximum amplitude of folding allowed. This ability to fold increases with generation and becomes significant from G₄ on, even allowing the branch to fold down to the core in the sixth generation. The folding of branches is seldom discussed in experimental papers. This is partly for two reasons. First, most of the experiments were reported for low generations, for which the amplitude of folding is small. Second, these dendrimers also do have elements of the scaffold that are permanently extended: the all-para branches.

In low generations, all the morphologies correspond to a dense-shell model, where layers of monomers are well-separated. But, as the generation increases, the ability of the branches to fold increases and the branches of the dendrons separate at the level of the inner layers, a behavior that can further favor the folding of the branches. As a result, the range of accessible morphologies also increases, from a dense-shell model to a model intermediate between a dense shell and a dense core (i.e., presenting a certain degree of mixing among monomers of different layers, channels, and cavities extending down to the core and most of the endgroups oriented outward). The morphological versatility can play an important role in the response of the molecule to external factors (solvent, solid-state interactions), such as when deposited on a surface: depending on the substrate and casting conditions, dendrimers were reported to organize as isolated molecules, aggregates, monolayers, fibers, or ribbons. Other critical factors affecting the morphology are the multiplicity and geometry of the core. Both define the growth directions of the persistent axes of the molecular scaffold.

Polyphenylene dendrimers were also built from A₄B monomers instead of A₂B monomers. The simulation results further highlighted the critical role of the branching pattern; the monomers have grafting points not only in the para and meta positions but also in the ortho position. The monomers grafted in the ortho position are forced to orient backward, which forces a mixing among the layers and decreases the conformational freedom. In addition, the number of monomers added at each generation shows a four-fold increase instead of a doubling, while the accessible molecular volume is unchanged. Both effects result in a dense packing limit reached at a very low generation, as early as G₂ for dendrimers built on a four-fold biphenyl.

These results highlight that the behavior of the polyphenylene dendrimers is more complex than initially thought. The general perception from earlier experimental and theoretical studies that polyphenylene dendrimers have a lower conformational freedom and are more rigid than the traditional flexible dendrimers remains globally valid. However, processes typical of flexible dendrimers, such as backfolding, can also take place in such dendrimers of high generation.

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