

Composition Rules for Omega Polynomial in Nano-Dendrimers

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Abstract. Omega polynomial $\Omega(G, x)$ counts the quasi orthogonal cut *qoc* strips in a graph $G=G(V, E)$. A *qoc* strip, defined with respect to any edge in G , represents the smallest subset of edges closed under taking opposite edges on faces. The first and second derivatives, in $x=1$, of Omega polynomial enables the evaluation of the Cluj-Ilmenau *CI* index. Dendrimers are hyper-branched macromolecules, with a rigorously tailored architecture. Because of their size, it is difficult to calculate this polynomial in high generation dendrimers. Thus, the composition of the global polynomial by monomeric contributions would enlighten the computational task. Composition rules for $\Omega(G, x)$ in nano-dendrimers, according to their topology, are derived. Counting formulas for the number of atoms and monomers in dendrimers grown at various generations are also given.

1. Introduction

Dendrimers are hyper-branched macromolecules, with a rigorous, aesthetically appealing architecture.¹⁻¹¹ They can be synthesized, in a controlled manner, basically by three strategies: (i) divergent; (ii) convergent and (iii) self-assembling ones.

In the *divergent methods*, dendrimers are built up starting from a core out to the periphery. In each repeated step, a number of monomer units react with the terminal groups of the already existing periphery to add a new shell or *generation*. By each successive generation the number of local coupling reactions increases. Examples of divergent synthesis can be found in refs.²⁻⁴

In the *convergent approach*, the synthesis of dendrimers starts from the periphery towards the central core. Large branched blocks (*i.e.*, dendrons, wedges), previously built up in iterative steps, are finally coupled to the core. In this case, the number of coupling reactions drops to the degree value of the core.⁵⁻⁷

The third approach comes from the combinatorial chemistry and/or nanoscience and makes use of building blocs, *i.e.*, monomers, able to join to each other in a limited number of ways.

These rigorously tailored structures reach rather soon a spherical shape, which resembles that of a globular protein. The size of dendrimers is in the nanometer scale. The endgroups (*i.e.*, the groups reaching the outer periphery) can be functionalized, thus modifying their physico-chemical or biological properties. Dendrimers have gained a wide range of applications in supra-molecular chemistry, particularly in host-guest reactions and self-assembly processes. Promising applications come from the polyamidoamine dendrimers as gene transfer vectors,^{12,13} but their applications are unlimited.

Molecular topology of dendrimers is a continuously developed topic. It includes vertex and fragment enumeration as well as calculation of some topological descriptors, such as topological indices, sequences of numbers or polynomials.^{1,14-20}

The present work aims to describe a dendritic polymer by composing the large molecule from its monomer(s), in terms of Omega polynomial. The article is organized as follows: The second section introduces in the topology of dendrimers, giving basic definitions and formulas to count the number of monomers on each dendritic generation or dendron and on the whole molecule as well. The third section illustrates the construction of nano-dendrimers from nanotube junction units, designed by using map operations. The fourth section provides the definition of Omega polynomial and details the way towards the factorization or composition of the polynomial and *CI* index, as well, in such hypothetical dendrimers. Conclusions and references will close the article.

2. Topological background

Before detailing the specific aspects of molecular topology in dendrimers, some basic definitions^{1,21-23} in the Graph Theory should be considered.

A *graph* $G(V,E)$ is an ordered pair of two sets, V and E , $V=V(G)$ being a finite nonempty set and $E=E(G)$ a binary relation defined on V . A graph can be visualized by representing the elements of V by points (*i.e.*, vertices) and joining pairs of vertices (i,j) by a bond (*i.e.*, edge) if and only if $(i,j) \in E(G)$. The number of vertices in G equals the cardinality $v=|V|$ of this set. A graph is said connected if any two vertices, i and j , are the endpoints of a path; otherwise it is disconnected. The vertex degree $d(i)$ is the number of edges incident in that vertex. If all the vertices in G show the same degree, the graph is called a d -regular graph.

A *walk* is an alternating sequence of vertices and edges $v_1, e_1, \dots, v_{n-1}, e_{n-1}, v_n$ in which any two subsequent vertices are adjacent (*i.e.*, $(v_i, v_{i+1}) \in E(G)$). Revisiting of vertices and edges of G is allowed. If the walk starts and ends in one and the same vertex (*i.e.*, $v_1=v_n$) the walk is a closed (or a self-returning) walk, otherwise it is an open walk. If no other conditions are imposed, the walk is called a random walk.

A *path* or a *self-avoiding walk* is the walk whose vertices are visited only once. Its vertices v_1, v_2, \dots, v_n are all-distinct and no branching is allowed. If the path joining the vertices i and j is a shortest one, it is called a *topological distance* or a *geodesic*. A *cycle* (or a circuit) is a closed path, thus being both self-returning and self-avoiding walk. A tree is a graph without cycles; it has either a monocenter or a dicenter (*i.e.*, two points joined by an edge).

Topology of dendrimers is basically that of a tree (*dendron* in Greek). Vertices in a dendrimer, except the external endpoints, are called branching points. The number of edges emerging from each branching point is called the *progressive degree*,¹ p (*i.e.*, the edges that enlarge the number of points of a newly added generation). It equals the classical degree, d , minus one: $p=d-1$.

A regular dendrimer has all branching points of the same degree, otherwise it is irregular. A dendrimer is called *homogeneous* if all its *radii* (*i.e.*, the chains starting at the core and ending in an external point) have the same length.

Accordingly, a dendrimer is called *monocentric* and *dicentric*, respectively. Examples are given in the Figure 1. The numbering of orbits (*i.e.*, generations) starts with zero for the core and ends with r , which is just the number of edges along the *radius* of the dendrimer.

A *wedge* is a fragment of a dendrimer (*i.e.*, a dendron) that may result either by breaking an edge in a dendrimer, or by a step of "convergent" construction. If the

cut edge ends at the core, the wedge is called *maximal*. The vertices of a wedge have the same degree as the corresponding ones in the whole dendrimer, except the cut point, whose degree is smaller by one.

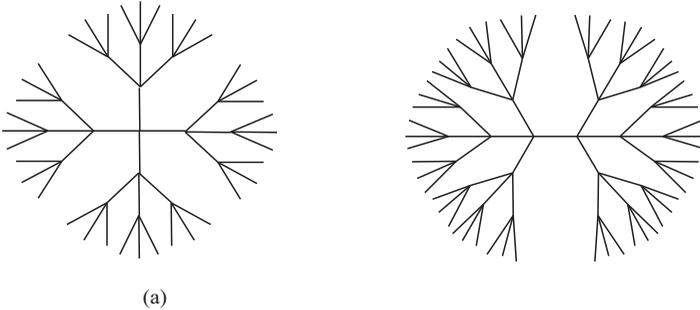


Figure 1. Monicentric (a) and dicentric (b) dendrimers, of generation $r=3$ and progressive degree $p=3$.

The stepwise growth of a dendrimer follows a mathematical progression. A first problem in studying the topology of dendrimers is that of enumerating its constitutive parts: vertices, edges or fragments.

The number of vertices in the i^{th} orbit (i.e., that located at distance i from the center) of a regular dendrimer can be expressed as a function vertex degree, d , and z

$$v_i = (2-z)(d+z-1)(d-1)^{(i-1)}; \quad i > 0 \quad (1)$$

where $z = 1$ for a monocentric dendrimer and $z = 0$ for a dicentric one. By using the progressive degree p , relation (1) becomes

$$v_i = (2-z)(p+z)p^{(i-1)}; \quad i > 0 \quad (2)$$

For the core, the number of vertices is: $v_0 = 2-z$, while the number of external vertices (i.e., the endpoints) are obtained by

$$v_r = (2-z)(p+z)p^{(r-1)} \quad (3)$$

where r is the radius of the dendrimer and equals the number of its orbits/generations.

The total number of vertices $v(D)$, in dendrimer, is obtained by summing the populations on all orbits

$$v(D) = (2-z) + (2-z)(p+z) \sum_{i=1}^r p^{(i-1)} \quad (4)$$

By developing the sum in (4) one obtains

$$v(D) = (2-z) + (2-z)(p+z) \left(\frac{p^r - 1}{p-1} \right) = \frac{2(p^{r+1} - 1)}{p-1} - zp^r \quad (5)$$

A useful recurrence enables one to calculate $v(D)$ from the number of vertices of the precedent term of a dendrimer family (*i.e.*, a homologous series of dendrimers, having the same progressive degree, p)

$$v(D_{r+1}) = pv(D_r) + 2 \quad (6)$$

irrespective monocentric or dicentric the dendrimer is.

The number of edges in a dendrimer equals $v(D)-1$, since it is a tree.

Vertices on a wedgeal fragment (*i.e.*, dendron), starting at the i^{th} orbit and ending at the periphery can be enumerated by

$$F_i = \sum_{s=i}^r p^{(r-s)} \quad (7)$$

The number of fragments (*i.e.*, wedges) starting at the i^{th} orbit equals the number of vertices lying on that orbit and can be calculated by relation (2).

3. Design of nano-dendrimer

The monomer on study in this paper is built up by using some map operations, namely the leapfrog Le and opening Op operations: Le(Le(Op(Le(T))))). In this respect, the reader is kindly addressed to consult the refs.²⁴⁻²⁸

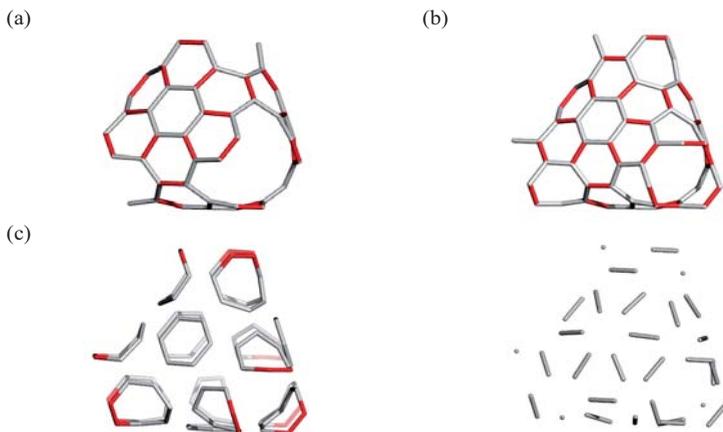


Figure 2. The monomer designed by Le(Le(Op(Le(T)))) map operations: (a) “jn” monomer, without heptagonal “negative” faces ($v=84$); (b) “id” monomer, with heptagonal faces ($v=108$); (c) Perfect Clar PC structure of monomer and (d) Fries associate structure.

Figure 2 illustrates two objects: “jn” monomer ($v=84$) and “id” monomer ($v=108$), corresponding to the “junction” and “identification” way, respectively, followed in the design of dendrimers. This figure also illustrates the perfect Clar PC structure²⁹ (c) and the associate Fries (d) structure³⁰ of this monomer. The nano-dendrimer, at the 1st and 2nd generation, respectively, are illustrated in Figure 3. Possible linear or circular evolution of the studied monomer is presented in Figure 4.

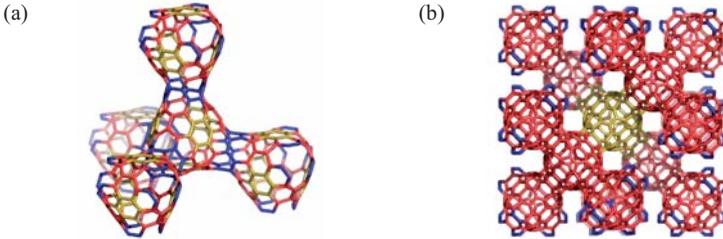


Figure 3. Nano-dendrimer at the stage/generation:

(a) 1st, $m=5$; $v=420$; $\Omega(D_{jn}, x) = 24x + 120x^3 + 30x^7$; $CI=350262$; “jn”-type

(b) 2nd, $m=17$; $v=1644$; $\Omega(D_{id}, x) = 420x + 408x^3 + 102x^7$; $CI=5551074$; “id”-type

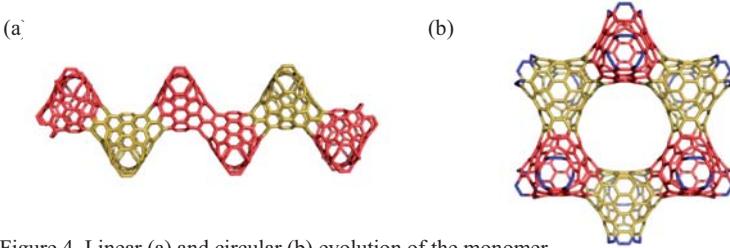


Figure 4. Linear (a) and circular (b) evolution of the monomer.

4. Omega polynomial in nano-dendrimers

Let $G(V,E)$ be a connected bipartite graph, with the vertex set $V(G)$ and edge set $E(G)$. Two edges $e = (x,y)$ and $f = (u,v)$ of G are called *codistant* (briefly: *e cof*) if

$$d(x,v) = d(x,u) + 1 = d(y,v) + 1 = d(y,u) \quad (8)$$

For some edges of a connected graph G there are the following relations satisfied:^{31,32}

$$e \text{ co } e \quad (9)$$

$$e \text{ co } f \Leftrightarrow f \text{ co } e \quad (10)$$

$$e \text{ co } f \ \& \ f \text{ co } h \Rightarrow e \text{ co } h \quad (11)$$

though the relation (11) is not always valid.

Let $C(e) := \{f \in E(G); f \text{ co } e\}$ denote the set of edges in G , codistant to the edge $e \in E(G)$. If relation co is an equivalence relation (i.e., $C(e)$ obeys (4) to (6)), then G is called a *co-graph*. Consequently, $C(e)$ is called an *orthogonal cut oc* of G and $E(G)$ is the union of disjoint orthogonal cuts: $C_1 \cup C_2 \cup \dots \cup C_k$ and $C_i \cap C_j = \emptyset$ for $i \neq j, i, j = 1, 2, \dots, k$. Observe co is a Θ relation, (Djoković-Winkler).³³⁻³⁵

A *quasi-orthogonal cut qoc* with respect to a given edge is the smallest subset of edges closed under taking opposite edges on faces. Since the transitivity relation (11) of the co relation is not necessarily obeyed, *qoc* represents a new concept within the cut methods. Any *oc* strip is a *qoc* strip but the reverse is not always true.

Let $m(G,c)$ be the number of *qoc* strips of length c (i.e., the number of cut-off edges); for the sake of simplicity, $m(G,c)$ can be written as m . The Omega polynomial is defined on the ground of *qoc* strips:^{36,37}

$$\Omega(G,x) = \sum_c m(G,c) \cdot x^c \quad (12)$$

Its first derivative (in $x=1$) equals the number of edges in the graph:

$$\Omega'(G,1) = \sum_c m \cdot c = e = |E(G)| \quad (13)$$

On Omega polynomial, the Cluj-Ilmenau³² index, $CI=CI(G)$, was defined:

$$CI(G) = \{[\Omega'(G,1)]^2 - [\Omega'(G,1) + \Omega''(G,1)]\} \quad (14)$$

It is easily seen that, for a single *qoc*, one calculates the polynomial: $\Omega(G,x) = 1 \times x^c$ and the index $CI(G) = c^2 - (c + c(c-1)) = c^2 - c^2 = 0$.

In tree graphs, the Omega polynomial simply counts the non-opposite edges, being included in the term of exponent $c=1$. The coefficient of the term of exponent $c=1$ has found utility as a topological index, called n_p , the number of *pentagon fusions*, appearing in small fullerenes as a destabilizing factor. This index accounts for more than 90 % of the variance in heat of formation HF of fullerenes C_{40} and C_{50} .³⁸

Composition of Omega polynomial in nano-dendrimers refers to the factorization according to the monomer description. The polynomial strictly follows the polygonal covering of structure and consists, according to the definition (12) of three terms. In case of “jn” dendrimer, the term at the highest exponent $c=7$ counts two joined coronene flowers, the number of which being 4 (as the number of faces in Tetrahedron); next, each flower shows exactly three strips, so that the coefficient is:

Table. Composition rules for Omega polynomial in the nano-dendrimers designed by Le(Le(Op(Le(T)))) operations.

Formulas	
1	$\Omega(D_{(4,3,m)}, x) = a_1 X^1 + a_3 X^3 + a_7 X^7$
2	$CI(D) = [\Omega'(D)]^2 - [\Omega'(D) + \Omega''(D)]$
“jn” Dendrimer	
3	$\Omega(D_{jn}, m, x) = 6(m-1)X^1 + 24mX^3 + 6mX^7$
4	$\Omega'(D_{jn}, 1) = 120m - 6; \Omega''(D_{jn}, 1) = 396m$
5	
6	$v(D_{jn}) = 84m$
7	$R[6](D_{jn}) = 28m; R[7](D_{jn}) = 6(m-1)$
“id” Dendrimer	
8	$\Omega(D_{id}, m, x) = [36 + 24(m-1)]X^1 + 24mX^3 + 6mX^7$
9	$\Omega(D_{id}, R, m, x) = [36 + 24(m-1) - 12R]X^1 + 24mX^3 + 6mX^7$
10	$;$ $\Omega''(D_{id}, 1) = 396m$
11	$CI(D_{id}) = 132 + 2778m + 138^2 \cdot m^2$
12	
13	$;$ $R[7](D_{id}) = 12m$
14	$m(r) = (p+1)p^{r-1}$
15	$m(D(p, r)) = 1 + (p+1) \sum_{i=1}^r p^{i-1} = \frac{2(p^{r+1} - 1)}{p-1} - p^r$

$a_7=4 \times 3/2=6$. The term at $c=3$ refers to two adjacent petals/hexagons of a coronene flower ending in two heptagons, each petal counting twice, hence: $a_3=2 \times 3 \times 4=24$. Finally, the term at power one counts the number of heptagonal rings, thus $a_1=R[7]$ (Table, rows 1 to 7). Formulas for CI , number of atoms v , and rings R are also given in Table. In case of “id” dendrimer, formulas take into account the additional heptagons at the terminal open faces (Table, entries 8 to 13). Entry 9 refers to ring containing structures, R being the number of rings. The number of monomers m in a nano-dendrimer is also given in Table, rows 14 and 15.

The prefix “nano” here express the complex structure of such hypothetical dendrimers, made of nanotube junctions. The reader is invited to consult our recent book³⁹ for a gallery of such junctions. Note worthy is these monomers, in the form of

hydrogenated ends, show excellent stability (total energy, HOMO-LUMO gap, strain and aromaticity), originating in the coronene moiety/flower; their structure shows a perfect Clar PC structure and an associate Fries structure (see Figure 2), both predicting a particular stability for such dendrimers. These results, which could be attractive for synthesists, will be published in a future article. Numerical evaluation of Omega polynomial was made by our software program Omega counter.⁴⁰

Conclusions

Dendrimers represent highly ordered hyper-branched structures reaching the nano-dimensions. Complex nano-dendrimers can be designed by using sequences of map operations. Because of their size, it is difficult to calculate our Omega polynomial $\Omega(G,x)$ in high generation dendrimers. Thus, the composition of the global polynomial by monomeric contributions would be welcome. Formulas for $\Omega(G,x)$ in nano-dendrimers, according to their topology, were derived. Counting formulas for the number of monomers in dendrimers grown at various generations were also given.

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