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Sadhana polynomial in nano-dendrimers

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ABSTRACT. Sadhana polynomial is defined on the ground of 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 derivative, in $x = 1$, of Sadhana polynomial is a multiple of the number of edges in the graph. Dendrimers are hyper-branched macromolecules, with a rigorously tailored architecture. In high generation dendrimers, it is difficult to calculate this polynomial. Thus, the composition of the global polynomial by monomeric contributions would facilitate the computation. Composition rule for in a family of nano-dendrimers, according to their topology, is derived.

1. INTRODUCTION

Dendrimers are hyper-branched macromolecules, with a rigorously tailored architecture [5], [29], [31], [37]-[41], [43]-[46]. They can be synthesized, in a controlled manner, either by a divergent or a convergent procedure. 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. Their applications in chemistry, biology and nano-science are unlimited. Dendrimers have been also studied from the topological point of view, including vertex and fragment enumeration and calculation of some topological descriptors, such as topological indices, sequences of numbers or polynomials [9]-[15], [25]. In the present work, a dendritic polymer composed by a well-defined monomer, is treated in terms of Sadhana 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 forth section provides the definition of Sadhana polynomial and its factorization according to the monomer contributions. Its relation with the Omega polynomial is derived. Conclusions and references will close the article.

2. TOPOLOGICAL BACKGROUND

Some basic definitions [16], [30], [47] in the Graph Theory should be considered.

A graph 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

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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.

The topological distance equals the number of traversed edges on the shortest path joining the vertices i and j; it is also called a geodesic. A cycle (or a circuit) is a closed path while a tree is a graph without cycles; a tree 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 [9], p (i.e., those edges that grow the number of points of a new generation). It equals the classical degree, d, minus one: $p = d - 1$.

A regular dendrimer has all branching points of the same degree d, 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, hereafter, the radius will be mentioned by a subscript $r : D_r$.

A dendrimer is monocentric or dicentric, the following dendrimers are regular and homogeneous of radius r see Figure 1, such dendrimer is called r-dendrimer.

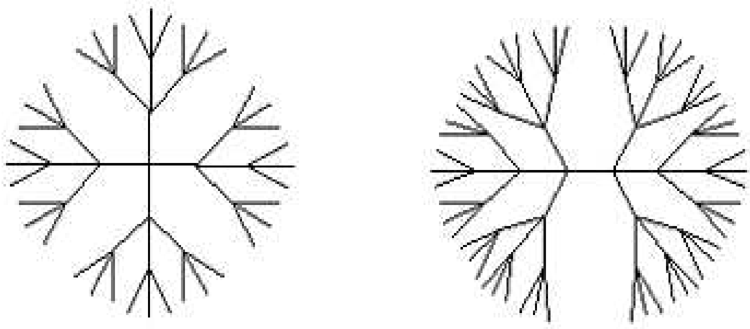

Figure 1. Monocentric (a) and dicentric (b) dendrimers, of generation r = 3 and progressive degree p = 3

The stepwise growth of a dendrimer follows a mathematical progression. 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

$$v_i(D_r) = (2 - z)(d + z - 1)(d - 1)^{(i-1)} \; i > 0 \tag{2.1}$$

where $z = 1$ for a monocentric dendrimer and $z = 0$ for a dicentric one. By using the progressive degree p, relation (2.1) becomes

$$v_i(D_r) = (2-z)(p+z)p^{(i-1)}\ i > 0 \tag{2.2}$$

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

$$v_r(D_r) = (2-z)(p+z)p^{(r-1)}, \tag{2.3}$$

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

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

$$v(D_r) = (2-z) + (2-z)(p+z)\sum_{i=1}^{r} p^{(i-1)}. \tag{2.4}$$

By developing the sum in (2.4) one obtains

$$v(D_r) = (2-z) + (2-z)(p+z)(\frac{p^r - 1}{p-1}) = \frac{2(p^{r+1}-1)}{p-1} - zp^r. \tag{2.5}$$

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.)

$$v(D_{r+1}) = pv(D_r) + 2 \tag{2.6}$$

irrespective monocentric or dicentric the dendrimer is.

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

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 [17]-[20].

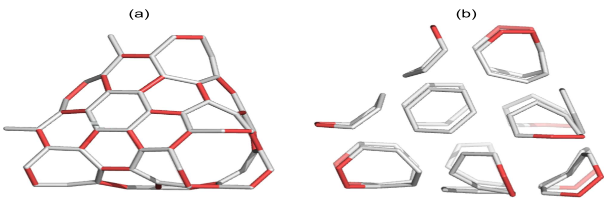

Figure 2. The monomer designed by Le(Le(Op(Le(T)))) map operations: (a) an ”id” monomer, with $v = 108$; (b) its associate Perfect Clar PC structure

Figure 2 illustrates the studied ’id” monomer ($v = 108$), used to design the nano-dendrimer by ”identification” of the ”open” faces of two up to $p + 1$ monomers. Its associate perfect Clar [7], [8] PC structure is also illustrated in this figure. The nano-dendrimer, at the 1st and 2nd generation, respectively, are illustrated in Figure 3.

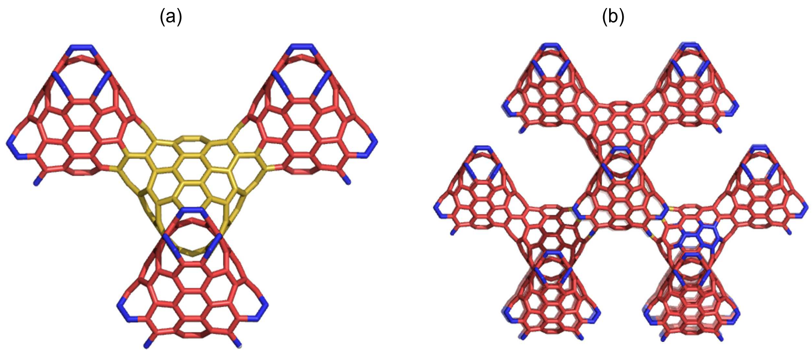

Figure 3. Nano-dendrimer at the stage/generation: (a) 1^{st}, m = 5, v = 492, e = 702, $Sd(D_{id}, x)$ = $132x$ + $120x^{699}$ + $30x^{695}$, $Sd' = 197262$, Sd'/e = 281. (b) 2^{nd}, $m = 17, v = 1644, e = 2358$, $Sd(D_{id}, x)$ = $420x^{2357}$ + $480x^{2355}$ + $102x^{2351}$, Sd'= 2190582 , $Sd'/e = 929$

4. Sadhana polynomial in nano-dendrimers

A quasi-orthogonal cut qoc with respect to a given edge is the smallest subset of edges closed under taking opposite edges on faces [21], [22].

Let $m(G, c)$ or simply m, be the number of qoc strips of length c (i.e., the number of cut-off edges). The Sadhana polynomial is defined on the ground of qoc strips [34], [35]:

$$Sd(G, x) = \sum_c m(G, c).x^{e-c} \tag{4.7}$$

with e being the cardinality of the edge set $e = |E(G)|$. This polynomial is based on a recently introduced 'Sadhana index', Khadikar et al. [4], [32]

$$Sd(G) = \sum_c m(G, c).(|E(G)| - c) \tag{4.8}$$

By definition of Omega polynomial [21], one can obtain the Sadhana polynomial by replacing x^c with $x^{|E|-c}$ in Omega polynomial. Then the Sadhana index will be the first derivative of $Sd(G, x)$ evaluated at $x = 1$. In fact, the first derivative (in $x = 1$) is a multiple of $e(G)$:

$$Sd'(G,1) = \sum_c m(G,c).(e-c) = \sum_c m(G,c)e - \sum_c m(G,c)c$$
$$= e\sum_c m(G,c) - e = e(\sum_c m(G,c) - 1) = e(Sd(G,1) - 1)$$

The relation of Sadhana index with Omega polynomial, out of the basic definition, is:

$$Sd(G) = Sd'(G,1) = \Omega'(G,1)(\Omega(G,1) - 1)$$

The Sadhana polynomial in nano-dendrimers can be factorized according to the monomer description. The polynomial strictly follows the polygonal covering of structure, as its pair polynomial Omega, and consists of three terms, according to three qoc strips:

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

No.	Formulas
1	$\Omega(D_{4,3,m}, x) = a_1X^1 + a_3X^3 + a_7X^7$
2	$Sd(D_{id}, x) = (24m + 12)X^{138m+11} + 24mX^{138m+9} + 6mX^{138m+5}$
3	$Sd'(D_{id}, 1) = (138m + 12)(54m + 11)$
4	$v(D_{id}) = 96m + 12$; $e = 138m + 12$
5	$R[6]D_{id} = 28m$; $R[7]D_{id} = 12m$;
	Number of monomers m at the stage/generation r
6	$m(r) = (p+1)p^{r-1}$
7	$m(D(p,r)) = 1 + (p+1)\sum_{i=1}^{r} p^{i-1} = \frac{2(p^{r+1}-1)}{p-1} - p^r$

A strip of $c = 7$ 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 $a_7 = 43/2 = 6$. A strip of $c = 3$ refers to two adjacent petals/hexagons of a coronene flower ending in two heptagons, each petal counting twice, hence: $a_3 = 234 = 24$. Finally, the last strip counts the number of "non-opposite" edges in the heptagonal rings, thus $a_1 = 334 + 24(m - 1) = 24m + 12$, because 12 edges are lost at each identification (see Table, entry 2). Formulas for the number of atoms v, edges e, rings R and the first derivative (in $x = 1$) are given in Table at entries 3 to 5. The number of monomers m in a nano-dendrimer is also given in Table (rows 6 and 7). We call these molecules "nano-dendrimers" to express their complex structure, made of nanotube junctions. The reader in invited to consult in this respect our recent books [23], [24].

Note that this monomer, in the form of hydrogenated ends, shows excellent stability (total energy, HOMO-LUMO gap, strain and aromaticity), originating in the coronene moiety/flower; their structure shows a perfect Clar PC structure (see Figure 2), which is associated with a Fries structure [28] (i.e., he valence structure showing the maximum number of benzenoid hexagons), both predicting a particular stability for such dendrimers. The number of Kekul valence structure, $K = 499392$, equals that of the fullerene C_{84}, numbered $20 - T_d$ in the Atlas of Fullerenes [27] All these results could be attractive for synthesists. Numerical evaluation of Sadhana polynomial and K-values were made by our software programs Omega counter and Kekul counter, respectively [6].

5. Conclusions

Complex nano-dendrimers can be designed by using sequences of map operations. Because of their size, it is difficult to calculate the Sadhana (or other counting) polynomial(s) in high generation dendrimers. The composition of the global polynomial by monomeric contributions would be an attractive way in facilitating the computational task. Formula for in a family of nano-dendrimers, according to their topology, was derived. Also given were formulas for counting the number of monomers in dendrimers grown at various stages.

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