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Determination of molecular weight and molecular radius of the polyamido carboxylic acid dendrimer using generation numbers

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ABSTRACT

Using of a Molecular equation of a first dendrimer surface and its relation to dendrimer molecular radios, it is possible to suggest the number of generation. Whereas a relative molecular weight is affiliated to the number of molecule formed in structural cells and on the other hand, structural cells have definite and determined dimensions, so by a simple replacement, the dendrimer molecular weight was directly related to its generation number. Data analysis derived from specific equation was shown that the prediction of a dendrimer molecular weight may be applicable by a specific generation.

Molecular weight of polyamido carboxylic acid dendrimer with specific number of generation could be theoretically estimated using the following eqs. (4) and (5).

$$y = \log M_w$$
$$= 2.0703 + 0.0844R_i \quad (4)$$
$$= 2.6339 + 0.4750G_n \quad (5)$$

R_i and G_n are molecular radius and number of generation respectively.

Such equations would result the molecular radius of the dendrimer. In this invented model there is no need to experiments and it can be key value to evaluate the experimental data.

1. Introduction

The dendritic structure is a widespread motif in nature often utilised where a particular function needs to be exposed or enhanced. Above ground, trees use dendritic motifs to enhance the exposure of their leaves to the sunlight, which is crucial to maintain life and growth via the photosynthesis. The shade of the tree crown creates a microenvironment maintaining higher humidity and more stable temperatures throughout the day compared to the surroundings. Also beneath ground, the trees have a maximum need to expose a large functional surface when collecting water from the soil. A large dendrite network of roots provides an excellent motif for that purpose (Fig. 1).

Dendrimers are a new class of synthetic polymers based on a well-defined cascade motif. These macromolecules may be synthesized to reach the size of Nan [2] objects having dimensions similar to proteins. Dendrimers allow a highly multivalent presentation of a given molecular motif in a highly defined fashion. In the early years of dendrimers, the synthetic approach to synthesis the two major dendrimer design, the poly propylene imines (PPI) and polyamido amine (PAMAM), polyamido carboxylic (PACA), relied on a stepwise "divergent" strategy in the divergent approach, the construction of the dendrimer take place in a stepwise manner starting from the core and building up the molecule towards the periphery using two basic operations coupling of the monomer and deportation or transformation of the monomer end-group to create a new reactive surface functionality and then coupling of a new monomer etc., in a monomer, somewhat similar to that know from solid-phase synthesis of peptides or oligonucleotides.

The processes of branching can be done in two methods: 1 → 2 and 1 → 3 [2,5]. In the branching method (1 → 2), the added monomer to the nucleus is activated in two points which is branched with two other branches. In the branching method (1 → 3), the monomer which is connected to the nucleus, have three active centers in order to branching [3,4,5,9].

By increasing of dendrimer generation, inaccessible free spaces (probe) is created for atoms in which geometric space molecular

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Fig. 1.

structure, molecular stability and the bond lengths and angles are responsible for it. These have been illustrated by the eq. (1)

$$A_{SAS} = 4\pi(R+P)^2 \quad (1)$$

in which, A_{SAS}, R and P are: the total surface, the radius and the inaccessible free spaces (probe radius) of the molecule of the PACA respectively.

Newkome and his colleagues shown the chaining rate of the square surface via probe radius (P) by the Fig. 2 [1].

The various of radius Probe (P) for the 5 and 6 generations has been nonlinear behavior then upper generations will had a linear behavior.

In 10 generation radius probe (P) was maximum value 10 Å. In this paper with have been P and R we will determinate of Molecular weight (M_w) PACA dendrimer.

2. Data analysis

Each dendrimer has specific molecular radius and hence with a specific occupied volume. Because of the existence of unoccupied volume in a dendrimer original volume of an unoccupied spaces is differ from a molecular with occupied spaces.

Newkom and coworkers has been shown a relation between total area (A_{SAS}) with radius probe and radius dendrimers. If radius

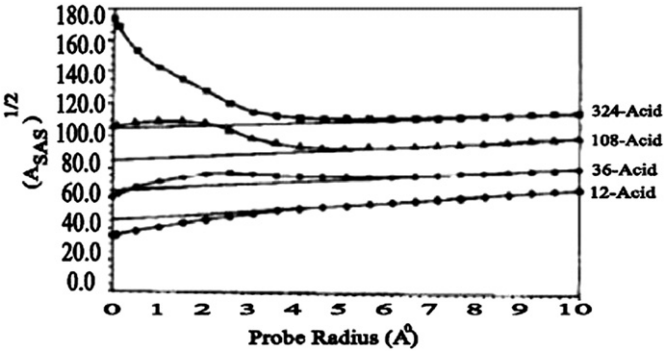

Fig. 2. Conversion of square surface via probe radius (P). Maximum P is 10 [1].

Table 1
Value of limited radius (R_i), molecular weight M_w, generation G of (PACA).

Generation	R_i	%GPR	Intercept eq. (4)	M_w R=CH_2NH_2	$y = \text{Log } M_w$
0	–	–	–	365	2.5623
1	12.7	78.7	45	1162	3.0652
2	18.3	54	65	3553	3.5506
3	24	50	85	10728	4.0305
4	29.6	33.8	105	32252	4.5086
5	35.3	28.4	125	96824	4.9860
6	40.1	22.3	145	290540	5.4632

probe was constant, then total area depends on only dendrimer radius. The slope and the intercept elevation of the eq. (2) are $2\sqrt{\pi}P$ and $2\sqrt{\pi}R$ respectively.

$$\sqrt{A_{ASA}} = 2\sqrt{\pi}R + 2\sqrt{\pi}P \quad (2)$$

If P is equal to zero then radius (R) converts to the limited radius (R_i).

The values of R_i was obtained eqs. (2) and (3).

The linear eq. (3) is resulted from by applying of R and G in Data Table 1.

$$R_i = 7.0333 + 5.6270G \quad (3)$$

For example, R_i could be obtained from the intercept in eq. (2) in generation one.

$$45 = 2\sqrt{\pi}(R_i) + 0 \Rightarrow R_i = \frac{15}{2\sqrt{\pi}} = 12.7$$

Also, for generation one using the eq. (3) R_i could be estimated.

$$R_i = 7.0333 + 5.6270G = 7.0333 + 5.6270(1) = 12.663$$

With respect to the existence of the probe radius in unoccupied volume of dendrimers. The percentage values of the probe radius (%GPR) could be obtained from the eq. (2) ie. for the generation one such volume was calculated.

$$\sqrt{A_{ASA}} = 2\sqrt{\pi}R + 2\sqrt{\pi}P_1 \Rightarrow 45 = 12.7 + 2\sqrt{\pi}P \Rightarrow P = 2.71$$

$$\%GPR = \frac{R_{i1} - P_1}{R_{i1}} \times 100 = \frac{12.7 - 2.71}{12.7} \times 100 = 78.7\%$$

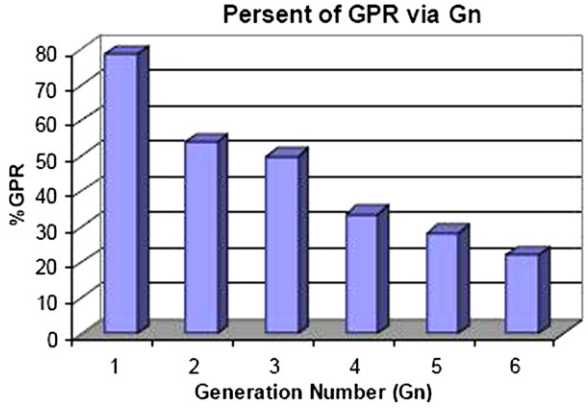

Fig. 3. The column chart of conversion percent of GPR via Generation number (G).

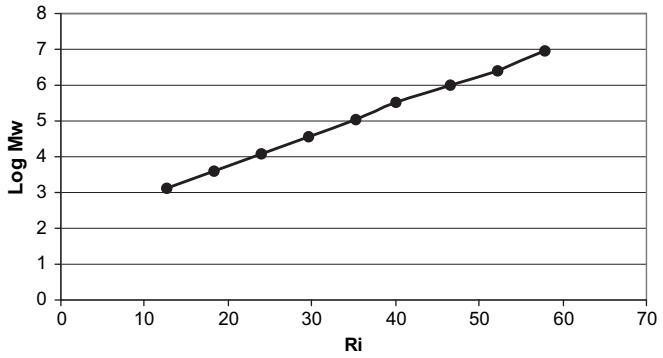

Fig. 4. Logarithmic variation of M_w regarded to limited radius.

R_{i1} and P_1 is limited radius and probe radius for the generation one respectively.

With attention to the experimental data in Fig. 2 [1], The P could not be estimated as zero, so it is possible to determine P for every generation using of the linear plot in eq. (2) Fig. 3, in which for the generation no.1 this value could be 2.71 Å. This can be done for the higher generations in which P_2, P_3, … are also obtainable.

By calculation of probe radius percentage for generation 1, The difference between the R_i (limited radius of its generation) and P_i might be calculated and the %GPR could be achieved. This showed that there are about 78.7% unoccupied spaces between the dendrimer molecules. With increasing of the generation number, %GPR is also decreased. This is 54% and 22.3% for generation no. 2 and no.6 respectively. It means that the unoccupied spaces are going to be diminished which is suggested to probable coiled wise shape of the molecule. The deviation of %GPR against generation number is illustrated in Fig. 3. It has been suggested that as the PACA is AB_2 type dendrimer, other AB_2 dendrimers like PPI And PAMAM may also behave in the same manner. For some of dendrimer molecules, in every generation there are inaccessibly empty spaces which is shown as Generation Probe Radius (GPR). Adverse relation of the GPR percent to the increasing of the generation number is shown in Fig. 3.

There is a decrease in percentage of conversion of GPR by increase generation number which has been shown in Table 1. This indicates that the occupied spaces by means of solvent are being decreased, and in other words,obtained polymer are more complex and more spherical. So the dendrimer radius is approach to the limited radius (R_i).

Using the data of Table 1 and plotting of log M_w against R_i the slope and intercept can be achieved those figure led us to extract a model eq. (4) Fig. 4.

$$y = \log M_w = 2.0703 + 0.0844R_i \tag{4}$$

Eq. (5) was confirmed with insertion of R_i (eq. (3)) in eq. (4).

$$\log M_w = 2.6639 + 0.4750G \tag{5}$$

3. Conclusion

It has been achieved that the molecular weight and limited radius of a dendrimer by foresaid generation number could be estimated (ie. by the means of eqs. (4) and (5)). Eq. (5) revealed that there is no need for the synthesis of higher generations of PACP dendrimers. So the molecular weight and the limited radius of PACA dendrimers are respectively obtained by substitution of generation number in eqs. (4) and (5).

Also obtaining of PACP dendrimers diameter with respect to the invented model, there is no need to achieve a molecular radius using experimental analysis such as scanning electron microscopy (SEM) and small angle neutron scattering (SANS) [6,7,8].

Another application of the invited model is the comparison of the molecular radius obtained by the computational and experimental techniques.

Will may lead us to create new models to apply in other dendrimers in future.

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