
SYNTHESIS OF DENDRIMER FROM ZINC METAL AND AMINO ACID PRESENT IN EGG ALBUMIN

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ABSTRACT

In this paper, synthesis of Dendrimer from the complex of transition metal Zn^{+2} with amino acid present in egg albumin is discussed. The complex so formed is analyzed on the basis of spectroscopic method of NMR and IR spectroscopy.

The above complex is decomposed at a temperature of $850^{\circ}C$ in muffle furnace to obtain a product of Dendrimer. This Dendrimer sample of product is then characterize by using scanning probe instruments STM, DLS, TEM and VSM.

Applications of dendrimers typically involve conjugating other chemical species to the dendrimer surface that can function as detecting agents, affinity ligands, targeting components, radioligands, imaging agents, or pharmaceutically active compounds.

Keywords- Amino acid, VSM, NMR, STM, DLS, TEM

INTRODUCTION

Nanoscience is the study of the properties of structures of the size smaller than several hundreds of nanometre (nm). Nanotechnology consists in techniques for designing and manufacturing these structures as well as applications arising from these. The development of nanoscience and nanotechnology is in line with the trend towards miniaturisation. Nanotechnology was first used to describe the extension of traditional silicon machining down into regions smaller than one micron (one millionth of a meter) by Tokyo Science University Professor Norio Taniguchi in 1974.

The **history of nanotechnology** traces the development of the concepts and experimental work falling under the broad category of [nanotechnology](#). Although nanotechnology is a relatively recent development in scientific research, the development of its central concepts happened over a longer period of time. The emergence of nanotechnology in the 1980s was caused by the convergence of experimental advances such as the invention of the [scanning tunneling microscope](#) in 1981 and the discovery of [fullerenes](#) in 1985, with the elucidation and popularization of a conceptual framework for the goals of nanotechnology beginning with the 1986 publication of the book [Engines of Creation](#). The field was subject to growing public awareness and controversy in the early 2000s, with prominent debates about both its [potential implications](#) as well as the feasibility of the applications envisioned by advocates of [molecular nanotechnology](#), and with governments moving to promote and [fund research](#) into nanotechnology. The early 2000s also saw the beginnings of commercial [applications of nanotechnology](#), although these were limited to bulk applications of [nanomaterials](#) rather than the [transformative](#) applications envisioned by the field.

The American [physicist](#) Richard Feynman lectured, "[There's Plenty of Room at the Bottom](#)," at an [American Physical Society](#) meeting at [Caltech](#) on December 29, 1959, which is often held to have provided inspiration for the field of [nanotechnology](#). Feynman had described a process by which the ability to manipulate individual atoms and molecules might be developed, using one set of precise tools to build and operate another proportionally smaller set, so on down to the needed scale. In the course of this, he noted, scaling issues would arise from the changing magnitude of various physical phenomena: gravity would become less important, surface tension and [Van der Waals attraction](#) would become more important.^[1]

After Feynman's death, scholars studying the historical development of nanotechnology have concluded that his actual role in catalyzing nanotechnology research was limited, based on recollections from many of the people active in the nascent field in the 1980s and 1990s. Chris Toumey, a cultural anthropologist at the University of South Carolina, found that the published versions of Feynman's talk had a negligible influence in the twenty years after it was first published, as measured by citations in the scientific literature, and not much more influence in the decade after the Scanning Tunneling Microscope was invented in 1981. Subsequently, interest in "Plenty of Room" in the scientific literature greatly increased in the early 1990s. This is probably because the term "nanotechnology" gained serious attention just before that time, following its use by K. Eric Drexler in his 1986 book, *Engines of Creation: The Coming Era of Nanotechnology*, which took the Feynman concept of a billion tiny factories and added the idea that they could make more copies of themselves via computer control instead of control by a human operator; and in a cover article headlined "Nanotechnology",^{[2][3]} published later that year in a mass-circulation science-oriented magazine, *OMNI*. Toumey's analysis also includes comments from distinguished scientists in nanotechnology who say that "Plenty of Room" did not influence their early work, and in fact most of them had not read it until a later date.^{[4][5]}

DENDRIMER

Dendrimers^[6] are repetitively **branched molecules**.^{[7][8]} The name comes from the **Greek** word **dendron**, which translates to "tree". Synonymous terms for dendrimer include **arborols** and **cascade molecules**. However, dendrimer is currently the internationally accepted term. A dendrimer is typically symmetric around the core, and often adopts a spherical three-dimensional morphology. The word **dendron** is also encountered frequently. A dendron usually contains a single chemically addressable group called the focal point or core. The difference between dendrons and dendrimers is illustrated in figure one, but the terms are typically encountered interchangeably.^[9]

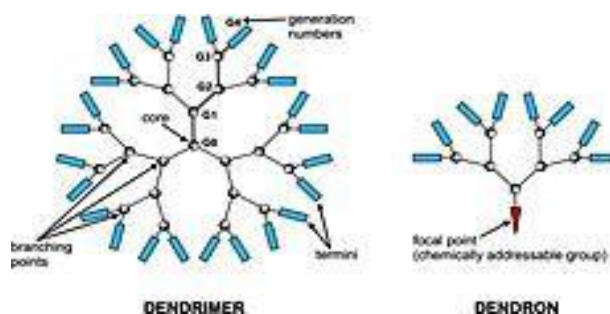


Figure 1: Dendrimer and dendron

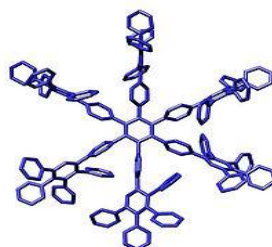


Figure 2: Crystal structure of a first-generation polyphenylene dendrimer

The structure of dendrimer molecules begins with a central atom or group of atoms labeled as the core. From this central structure, branches of other atoms called 'dendrons' grow through various chemical reactions.

The continuous branching results in layers of branch structure called “generations.” Another way to determine the generation of a dendrimer is through the total number of focal or branching points (from the core to the surface) that it has. For example, a dendrimer with 4 focal points would be a fourth generation dendrimer, labeled as G4. There is a myriad of generations, ranging from just a few to hundreds or even thousands. As the molecule grows bigger, the structure becomes denser and more tightly packed. Eventually, the branches cannot grow any further because there is no room. The generation at which this occurs is different for every molecule, but it is known as the starburst effect. The shape of lower generation molecules (such as G0, G1, and G2), tend to be asymmetrical, but as the generation number increases, the structure becomes more spherical. Other components of dendrimers include the shell (segment between focal points), and the end-group (the atoms that make up the surface of the molecule).

The first dendrimers were made by divergent synthesis approaches by [Fritz Vögtle](#) in 1978,^[10] [R.G. Denkewalter](#) at [Allied Corporation](#) in 1981,^{[11][12]} [Donald Tomalia](#) at [Dow Chemical](#) in 1983^[13] and in 1985,^{[14][15]} and by [George Newkome](#) in 1985.^[16] In 1990 a convergent synthetic approach was introduced by [Jean Fréchet](#).^[17] Dendrimer popularity then greatly increased, resulting in more than 5,000 scientific papers and patents by the year 2005.

PROPERTIES

Dendritic molecules are characterized by structural perfection. Dendrimers and dendrons are monodisperse and usually highly symmetric, spherical compounds. The field of dendritic molecules can be roughly divided into low-molecular weight and high-molecular weight species. The first category includes dendrimers and dendrons, and the latter includes dendronized polymers, hyperbranched polymers, and the polymer brush. The properties of dendrimers are dominated by the functional groups on the molecular surface, however, there are examples of dendrimers with internal functionality.^{[14][15][16]} Dendritic encapsulation of functional molecules allows for the isolation of the active site, a structure that mimics that of active sites in biomaterials.^{[17][18][19]} Also, it is possible to make dendrimers water-soluble, unlike most polymers, by functionalizing their outer shell with charged species or other hydrophilic groups. Other controllable properties of dendrimers include toxicity, crystallinity, tecto-dendrimer formation, and chirality.^[4]

SYNTHESIS

One of the very first dendrimers, the Newkome dendrimer, was synthesized in 1985. This [macromolecule](#) is also commonly known by the name arborol. Figure 3 outlines the mechanism of the first two generations of arborol through a divergent route (discussed below). The synthesis is started by [nucleophilic substitution](#) of 1-bromopentane by *triethyl sodiomethanetricarboxylate* in [dimethylformamide](#) and [benzene](#). The [ester](#) groups were then [reduced](#) by [lithium aluminium hydride](#) to a [triol](#) in a [deprotection](#) step. Activation of the chain ends was achieved by converting the alcohol groups to [tosylate](#) groups with [tosyl chloride](#) and [pyridine](#). The tosyl group then served as [leaving groups](#) in another reaction with the tricarboxylate, forming generation two. Further repetition of the two steps leads to higher generations of arborol.^[12]

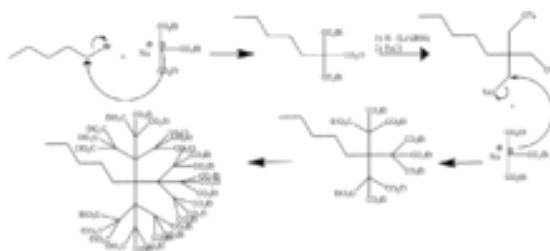


Figure 3: Synthesis to second generation arborol

Poly(amidoamine), or PAMAM, is perhaps the most well known dendrimer. The core of PAMAM is a diamine (commonly ethylenediamine), which is reacted with methyl acrylate, and then another ethylenediamine to make the generation-0 (G-0) PAMAM. Successive reactions create higher generations, which tend to have different properties. Lower generations can be thought of as flexible molecules with no appreciable inner regions, while medium-sized (G-3 or G-4) do have internal space that is essentially separated from the outer shell of the dendrimer. Very large (G-7 and greater) dendrimers can be thought of more like solid particles with very dense surfaces due to the structure of their outer shell. The functional group on the surface of PAMAM dendrimers is ideal for click chemistry, which gives rise to many potential applications.^[21]

MATERIALS AND METHOD

To obtain a Dendrimer product, 0.5 normal metal salt, Zn^{2+} solution was prepared in ethyl alcohol. It is allowed to react with egg albumin to form a complex of egg albumin with zinc ion. The metal -albumin complex, so formed was, decomposed at higher temperature as reported in the literature.

PREPARATION OF AMINO ACID-METAL COMPLEX

As we know that proteins are macromolecules comprising of amino acid as monomer. Amino acid is compound containing $-NH_2$ and $COOH$. With the help of these groups, amino acids form complexes with metal and different chains of amino acids combined together. These compounds on decomposition give carbon metal nano tubes.

When aqueous solution of Zinc salt is allowed to react with amino acid present in egg albumin the lone pair present on nitrogen of $-NH_2$ and oxygen of COO^- of $COOH$ group present in amino acid forms complex with zinc. In this Zinc (II) forms cross links between two amino acid chains.

The structure of albumin is very complex and it is very difficult to produce exact structure of amino acid-metal complex. Egg albumin contains a number of different chemical compounds for example.

Egg albumin contain Arginine $-(NH_2 - C(CH_2)_3 CH(NH_2) COOH)$ and lysine $(NH_2(CH_2)_4 CH(NH_2) COOH)$ amino acids. They react with Zinc metal solution to give the following complexes.

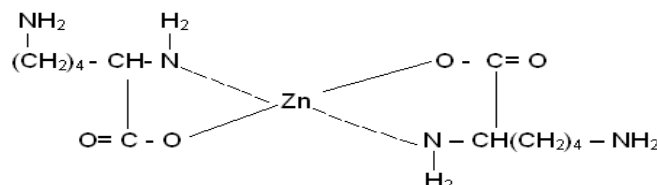


Fig.4 Lysine – Zinc (II) Complex

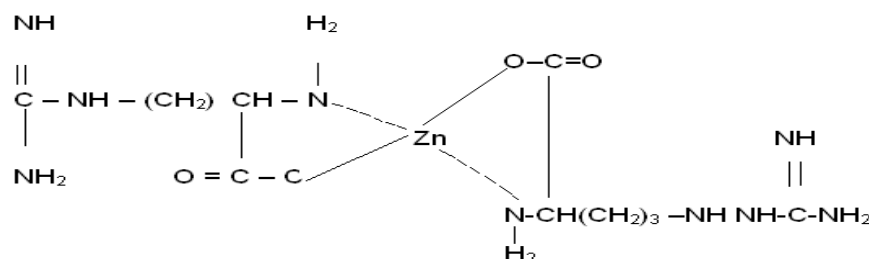


Fig.5 Arginine -Zinc (II) Complex

CURRENT APPLICATIONS

Today, dendrimers have many medicinal and practical applications. Firstly, they are used in cardiac testing. In this method, proteins from a blood sample are attached to glass by dendrimers. The result tells if there is any muscle damage, and significantly reduces the testing time from 40 minutes to 8. Dendrimers are also used as contrast agents in MRIs (Magnetic resonance imaging). Contrast agents improve sensitivity and specificity during the imaging process.

Result and Discussion-

Characterization:-

(a) Characterization of complex-

The complex between Zn^{2+} and egg albumin so formed is characterized by NMR and I R spectroscopy.

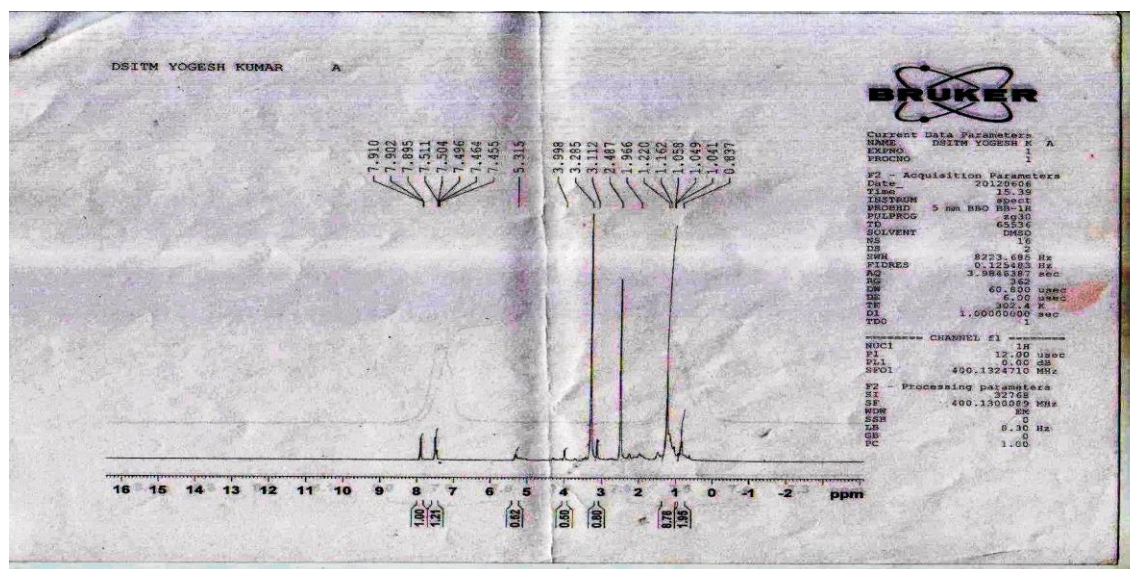


Figure 6 NMR Spectra of zinc salt and egg protein in alcoholic medium

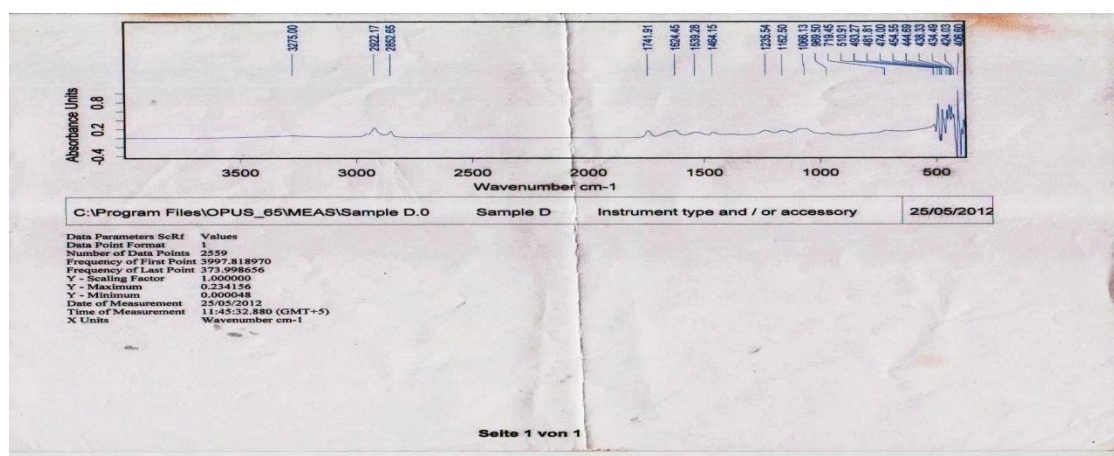


Figure 7 IR Spectra of Zinc salt and egg protein in alcoholic medium

(b) Decomposition of the complex of Zn^{2+} and egg albumin:-

The complex is decomposed in the muffle furnace at $850^{\circ}C$. The decomposed sample has been characterized using scanning probe instrument such as, AFM SEM etc. A magnetic behavior has been established.

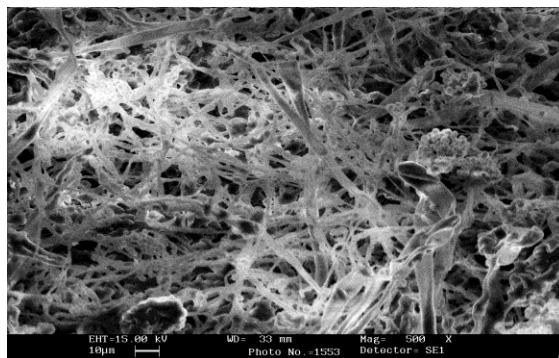


Figure 8 SEM image of sample of complex of egg albumin and Zn_2^+ Dendrimer in Alcoholic medium

From SEM study, it is clear from figure 8 that Dendrimer is formed.

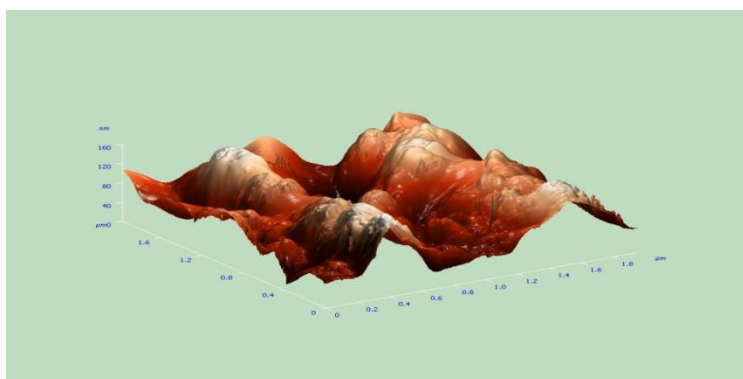


Figure 9 AFM image of decomposed sample of Zn^{2+} egg albumin complex at $850^{\circ}C$ temperature

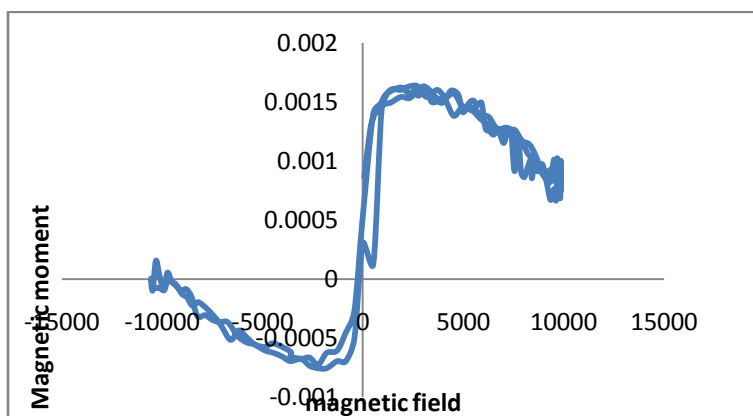


Figure 10 VSM Graph of Sample prepared by using zinc salt and Egg protein in alcoholic medium:

AFM study also shows dendrimer structure figure 9.

Magnetic behavior from VSM study the sample is found to be di-magnetic behavior figure 10.

CONCLUSION:-

From AFM, SEM study, it is clear that Dendrimer has been formed.

VSM study tells about the di-magnetic behavior of Dendrimer

REFERENCES-

1. Gribbin, John; Gribbin, Mary (1997). *Richard Feynman: A Life in Science*. Dutton. p. 170. ISBN 0-452-27631-4.
2. Hapgood, Fred (November 1986). ""Nanotechnology" / "Tinytech"". *Omni*: 56.
3. Drexler, Eric (15 December 2009). "[The promise that launched the field of nanotechnology](#)". *Metamodern: The Trajectory of Technology*. Retrieved 13 May 2011.
4. Toumey, Chris (2005). "Apostolic Succession". *Engineering & Science* **1/2**: 16–23.
5. Toumey, Chris (2008). "Reading Feynman into Nanotechnology: A Text for a New Science". *Techné* **13** (3): 133–168.
6. <http://cycuimingming.blog.com/2014/06/19/174/>.
7. D. Astruc, E. Boisselier, C. Ornelas (2010). "Dendrimers Designed for Functions: From Physical, Photophysical, and Supramolecular Properties to Applications in Sensing, Catalysis, Molecular Electronics, and Nanomedicine". *Chem. Rev.* **110** (4): 1857–1959. doi:10.1021/cr900327d.
8. Vögtle, Fritz / Richardt, Gabriele / Werner, Nicole *Dendrimer Chemistry Concepts, Syntheses, Properties, Applications* 2009 ISBN 3-527-32066-0.
9. Nanjwade, Basavaraj K.; Hiren M. Bechraa; Ganesh K. Derkara; F.V. Manvia; Veerendra K. Nanjwade (2009). "Dendrimers: Emerging polymers for drug-delivery systems". *European Journal of Pharmaceutical Sciences* (Elsevier) **38** (3): 185–196. doi:10.1016/j.ejps.2009.07.008. PMID 19646528.
10. D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder and P. Smith (1985). "A New Class of Polymers: Starburst-Dendritic Macromolecules". *Polymer Journal* **17**: 117–132. doi:10.1295/polymj.17.117.
11. [Treelike molecules branch out - chemist Donald A. Tomalia synthesized first dendrimer molecule - Chemistry - Brief Article](#)". *Science News*. 1996.
12. George R. Newkome, Zhongqi Yao, Gregory R. Baker, Vinod K. Gupta (1985). "Micelles. Part 1. Cascade molecules: a new approach to micelles. A [27]-arborol". *J. Org. Chem.* **50** (11): 2003–2004. doi:10.1021/jo00211a052.
13. Hawker, C. J.; Fréchet, J. M. J. (1990). "Preparation of polymers with controlled molecular architecture. A new convergent approach to dendritic macromolecules". *J. Am. Chem. Soc.* **112** (21): 7638–7647. doi:10.1021/ja00177a027.
14. Antoni, P.; Hed, Y.; Nordberg, A.; Nyström, D.; Hult, A.; Malkoch, M. (2009). "Bifunctional Dendrimers: From Robust Synthesis and Accelerated One-Pot Postfunctionalization Strategy to Potential Applications". *Angew. Int. Ed.* **48** (12): 2126–2130. doi:10.1002/anie.200804987. PMID 19117006.
15. McElhanon, J. R.; McGrath, D. V. (2000). "Toward Chiral Polyhydroxylated Dendrimers. Preparation and Chiroptical Properties". *JOC* **65** (11): 3525–3529. doi:10.1021/jo000207a.
16. Liang, C. O.; Fréchet, J. M. J. (2005). "Incorporation of Functional Guest Molecules into an Internally Functionalizable Dendrimer through Olefin Metathesis". *Macromolecules* **38** (15): 6276–6284. doi:10.1021/ma050818a.
17. S. Hecht, J. M. J. Fréchet (2001). "Dendritic Encapsulation of Function: Applying Nature's Site Isolation Principle from Biomimetics to Materials Science". *Angew. Chem. Int. Ed.* **40** (1): 74–91. doi:10.1002/1521-3773(20010105)40:1<74::AID-ANIE74>3.0.CO;2-C. PMID 11169692.