3D aerosol printing as method to obtain low-temperature ceramic layers of printed circuit boards

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Abstract. A method for the synthesis of the polyaluminosilicates (PAS) with the macromolecules of dendrimer morphology has been developed. A quantum-chemical assessment of thermodynamically possible mechanisms to develop the populations of short-chain aluminosilicates (nuclei of dendrimer macromolecules) has been carried out followed by the domains generation from the dendrimer assemblies capable to contain up to 80 % wt of the dispersed filler particles into their interdomain spaces by means of the GAUSSIAN B3LYP/6-31G (d) software package. A quantitative calculation of the parameters determining the composition of PAS macromolecules and the size of the dendrimer assemblies has been carried out. A method for the synthesis of monomeric precursor-powder has been developed. A new low-temperature ceramic composite material for 3D aerosol printing has been developed on the basis of the PAS and highly dispersed precursor-powder. The processes of 3D aerosol printing of the PAS filled with monomeric precursor-powder have been researched. An optimal method for aerosol generation has been chosen that does not affect the PAS supramolecular structure. The ceramic dielectric layers with high consumer properties have been obtained by means of 3D aerosol printing.

1. Introduction
Microelectronic products and spacecraft devices with a long active service period based on multifunctional structural materials can be successfully developed provided that the new generation polymer composite material is created. The main problem is the heat dissipation while using such products. The importance to develop materials with high thermal conductivity, resistance to aggressive environments, high temperatures and their significant differences, various radiations, high vacuum, and high pressures becomes more urgent with increasing human activity.

Nowadays there is an important task to apply such new composite materials on the surfaces of various products and devices along with the problem to develop them in many industries. 3D printing is the modern method to form various coatings and topologies in different products and devices, including microelectronics.

Nowadays it is not always possible to obtain the homogeneous nanostructured ceramic coatings with a specific microstructure, high purity, high thermal conductivity, and simultaneously with a rational stoichiometry. That is why the development of microprinting technology is limited to the technologies for producing consumable products with the necessary functional and structural
properties, as well as a thorough physicochemical and morphological analysis of the obtained polymer matrices and their components.

The role of the controlled chemical synthesis of the substances for ceramic materials that form multilayer coatings is decisive to solve the problem. The reason is that nanosize, phase, structural, and other features that determine the physical, mechanical, chemical, and operational properties of end coatings for microelectronic products and spacecraft devices with a long active service period under severe operating conditions form at the synthesis stage. This problem is to a large extent limited to the synthesis and chemical modification of various functionalized nanoparticles with the set chemical and phase composition and morphology and also to the study of such particles behavior in the initial matrix and in the process of solvent removing from a limited volume of a microdroplet [1].

Nowadays many high-tech companies all over the world switch to the technology of prototyping and commercial production of modern microelectronic and spacecraft devices using computer design and microprinting. It is not possible to obtain a specific dielectric layer or topology with the set thermophysical, physical, and chemical properties at the certain area of a device or product by means of traditional methods with the use of commonly applied materials because metallic and nonmetallic materials commonly applied in various industries have to a great extent reached their functional and structural limits.

Physical chemistry of high-molecular compounds is rapidly developing in the frame of fundamental science and different technologies. It is a new field concerned with the synthesis and study of the structure and properties of three-dimensional hyperbranched polymers and oligomers, the so-called dendrimers (fractals) [2]. The materials with such macromolecular assembly morphology attract our attention because the number of branches increases exponentially by each chain growth act in three-dimensional macromolecular assembly synthesis. As a result, the macromolecule size and shape change that leads to major physical and physicochemical properties change such as viscosity, solubility, moisture absorption, density etc.

Thus, special synthetic approaches allow obtaining regular dendrimer assemblies (DA), the macromolecules of which have a well-defined molecular weight. Furthermore, it should be noted that a lot of physical and physicochemical properties of dendrimer materials such as glass transition temperature mainly depend on the chemical nature of the terminal groups located on such spherical macromolecules-fractals.

The modern and available method to produce functional and structural materials with the necessary properties is currently a sol-gel technology that allows controlling the chemical nature of the material in the synthesis phase, thereby setting the required properties for the finished composites. The sol-gel technology is the primary method to obtain multipurpose nanodispersed materials. The actual tendency of sol-gel synthesis is to modify the siliceous compounds by both organic and inorganic substances. The sol-gel method peculiarity is the hydrolytic polycondensation reaction of alkaline silicates that occurs in the presence of inorganic substances (salt, acid) and low and high molecular organic modifiers. They give the specified physicochemical and technically essential properties to the formed materials. As a rule, the inorganic substances and modifiers are template agents contributing to the formation of silicate and hybrid nanocomposites with a specific structure [3-8].

The primary task is to apply the obtained material on different in their chemical nature bases and study the processes that occur when applying the obtained material. This task is to be solved along with the basic task to produce new ceramic composite materials with specified functional and structural properties used as consumable products for 3D printing of various coatings and topologies in microelectronic devices and products. Such process task as layers and topologies application generates current scientific challenges of surface physical chemistry, for example, the problem of material adhesive power and strength. Simultaneously, applying material on the product or device surface generates fundamental research of physicochemical processes.

Currently there are many methods of additive printing of composite materials that relate to printing technology. The printing technology development is based on the achievements in the field of nanotechnology and nanomaterials. Consequently, the production of functional elements with the use
of a printer relates to nanoelectronics. Research and development in this field of nanotechnology is a crucial task because it is dynamically developing now.

2. Experiment

2.1. Composite material obtaining

One of the study objectives related to physical chemistry of high-molecular compounds is to study how the PAS chemical structure influences on the macromolecule sizes and conformations. The molecular dendrimer (fractal) system is a regularly branched tree-shaped structure. The main unit of their macromolecules are crowns (dendrons). The combination of crowns in one central unit leads to the formation of dendrimers, the macromolecules of which have a close to spherical shape (figure 1). The crown inclusion in the repeating units of linear polymers allows obtaining fractal polymers or, as they are often called, cylindrical dendrimers. The possibility to obtain the terminal groups of macromolecules controlled by chemical structure, size, and number, as well as to modify them by varying the crown generation number and physicochemical structure of the terminal fragments allows solving the fundamental problems of physical chemistry of complex branched molecular systems and developing new functional materials for microelectronics. It seems to be important to research comprehensively the influence of the generation number, chemical structure of the crown and end groups on the sizes and conformations of dendrimer macromolecules and crown-modified polymers in the polymer systems filled with highly dispersed fillers.

![Figure 1. TEM photograph of dendrimers of PAS macromolecular assemblies (200 nm scale, Philips CM 30 transmission electron microscope).](image1)

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![Figure 2. Models of oligomer PAS conformers that are able to play role of nuclei in dendrimer assemblies and participate in crown formation (visualized by GAUSSIAN computer program). Viscosity has been measured by Brookfield DV2TRV viscometer. (a) – viscosity 1560 cPs, (b) – viscosity 2134 cPs, (c) – viscosity 1873 cPs, (d) – viscosity 1947 cPs.](image2)

**Figure 2.** Models of oligomer PAS conformers that are able to play role of nuclei in dendrimer assemblies and participate in crown formation (visualized by GAUSSIAN computer program). Viscosity has been measured by Brookfield DV2TRV viscometer. (a) – viscosity 1560 cPs, (b) – viscosity 2134 cPs, (c) – viscosity 1873 cPs, (d) – viscosity 1947 cPs.
A silicic acid and aluminum nitrate have been chosen as starting reagents to form the dendrimer PAS assemblies for the dendrimer PAS synthesis to obtain the filled tailored materials. The formation has been carried out in three stages: I stage: the silicic acid dissolution by the pH > 7; II stage: the aluminum nitrate hydrolysis; III stage: the light polycondensation with gel-precursor formation from oligosilicic acids and \( \text{O}_3\text{N-Al-(OH)}_2 \) [3].

Depending on the number of initial components used for the synthesis and polycondensation reaction temperature we have obtained the PAS with a different structure of the polymer chain (figure 2) having different viscosity (characterized by a molecular weight) and able to accommodate different amounts of disperse filler in their interdomain spaces.

A simple comparison of the visualized models images (calculated by the quantum-chemical method) (figure 2) and the microphotograph of the dendrimer PAS assembly obtained by a transmission electron microscope (TEM) (figure 1) allows us to conclude that the morphological picture of the obtained PAS is identical with the one obtained by TEM and the participation of oligomer segments in crown formation. In other words, the formation of PAS macromolecules begins with the formation of a dendrimer nucleus, on which other arcuate oligomer segments are grown in spatially accessible OH-groups. As a result, the macromolecules form, i.e. the dendrimers that are clearly seen on the TEM image (figure 1).

The study of the PAS chemical structure begins with the study of viscosity characteristics and the effect of the dendrimer macromolecule generation number on the behavior of the terminal groups that form the crown of a PAS domain. The limiting sizes, configuration, and molecular weight characteristics of regular dendrimers can be theoretically predicted by means of the quantum-chemical assessment of the conformations of the initial PAS oligomer compounds (figure 2).

Since the growth of crown generations in all directions is equally probable, they take a close to spherical shape after 3 or 4 generations. However, it should be taken into account that the crown thickness increases with an increase in the generation number of the dendrimer macromolecule. The crown size increasing is characterized by the unfolding of the terminal chains in the radial direction of the macromolecules. Such a steric effect is possible due to the interactions occurring between the terminal chains due to the dendritic migration surface area decrease per one crown as they increase in the macromolecule. Consequently, an increase in the generation number \( G \) stimulates the terminal groups self-organization that tend to transit to the PAS dendrimer macromolecule outer layer. Then since all the macromolecules increase in their molecular weight by the same amount at each stage of the PAS controlled synthesis, an almost monodispersed PAS forms as a result.

2.2. The synthesis of monomeric precursor-powder

The synthesis of monomeric precursor-powder has been carried out by doping. It is doping that is one of the ways to obtain powders with a nanosized structure at the lowest cost. The synthesis is based on the chemical plating method.

At the first stage, \( \text{Al}(\text{NO}_3)_3 \times 9\text{H}_2\text{O} \) has been chosen as an initial reagent. The method of reverse plating has been used to ensure the maximum completeness of plating components and high degree of the plate homogeneity.

The following points have been taken into account by the plating:

- the diluted solutions of salts and a precipitator have been used (~0.12 M);
- the feed rate of the salt solutions has been chosen so that pH during the plating is ~9.2;
- plating has been carried out at a temperature of minus 6 °C and with thorough stirring;
- the plating time in the mother solution has been minimal after the plating completion in order to slow the growth of agglomerates.

The second stage of the synthesis has been the ultrasonic treatment of the obtained plates in order to decrease their agglomeration degree. Then the deagglomerated plates have been processed at a temperature of minus 25 °C (20 hours) that allowed carrying out the deep dehydration of the plates and preserve the formed nano-dimensions of the co-plated powders. According to the sedimentation analysis, the agglomerate size in the co-plated powders is 20–40 nm after freezing (figure 3).
2.3. The monomeric precursor-powder injection into the PAS matrix

After viscometric measurements of the synthesized PAS, the distances between the chain ends of the macromolecules segments $L$ have been calculated. The conformer geometry and shape have been assessed by the quantum-chemical optimization methods of the geometry and energy of possible molecular assemblies-segments that are the products of PAS oligomerization. The distances $L = 15.11$ Å (angstroms) for the conformer $a$ (figure 2(a)), the distances $L = 37.13$ Å for the conformer $b$ (figure 2(b)), the distances $L = 28.39$ Å for the conformer $c$ (figure 2(c)), distances $L = 28.66$ Å for the conformer $d$ (figure 2(d)). The conformer $a$ is the most probable conformer involved in strong branching (crown formation) of the aluminosilicates, since the crown size increase is characterized by the unfolding of the end chains in the radial direction of the macromolecules. Although the distance between the ends of the conformers $c$ and $d$ is only 1.8 times larger than that of the conformer $a$, the process of PAS polycondensation with the formation of linear macromolecules is difficult. Consequently, the results of the quantum-chemical calculations correlate with the data of the experimentally obtained viscometric measurements.

One controls the supramolecular dendrimer assemblies by regulating the quantitative characteristics defining their microstructure and size according to certain parameters, such as the number of spatial segments of branches from generations or crowns ($N_c$), the number of branches formed by each spatial segment or the branching index of links ($N_b$), the number of terminal groups ($Z$), the number of generations ($G$).

We have analyzed the dendrimer supramolecular formations of the synthesized aluminosilicates according to the scheme (figure 4) and have calculated the polymerization degree ($P$), $N_c$, $N_b$ and $G$ for the conformer $a$ as for the most probable one. The values obtained for the conformer $a$ are the following: $N_c = 3$, $N_b = 3$ and $G = 3$. The polymerization degree $P$ or number of repeating units with $N_c = 3$, $N_b = 3$ and $G = 3$ have been calculated according to the equation (1) that has the value 120 ($P = 120$).

$$P = N_c \cdot N_b^{G+1} - 1 \over N_b - 1$$

(1)

The number of terminal groups is 81 ($Z = 81$) and has been calculated according to the equation (2).

$$Z = N_c \cdot N_b^G$$

(2)

The molecular weight of the amorphous dendrimer PAS $M$ is $\sim 480000; M_i = M_a \sim 1300$. The value $M$ has been calculated according to the equation (3).
\[ M = M_c + N_c \left[ \frac{M_u \cdot \left( N_b^{G+1} - 1 \right)}{N_b - 1} + M_t \cdot N_b^{G+1} \right], \]  

(3)

where \( M_c \) – the molecular weights of the nucleus, \( M_u \) – repeating unit formed from the initial compounds and \( M_t \) – terminal group.

The regularity violations in the structure of the supramolecular PAS formations and the lack of predictability may be caused by the traditional reaction mechanism violation, such as the presence of side intramolecular reactions, incomplete targeted reactions due to steric difficulties arising from the substituents accumulation etc. However, it is considered that the branching regularity violations in dendrimer macromolecules do not dramatically affect their size. This is confirmed by the experiments, in which the dendrimers structure regularity has been deliberately violated. The same conclusion can be made from the data on the measurement of the macromolecules size of the dendrite-like polymers obtained by the method of one-stage synthesis.

**Figure 4.** Scheme of controlled synthesis of dendrimers.

We have analyzed the elemental composition of the dendrimer PAS by the X-ray fluorescence spectroscopy to confirm quantitatively the calculated degrees of the polymerization and molecular weight (table 1).

| Element | X-ray fluorescence analysis (%) | Computer experiment (%) |
|---------|--------------------------------|------------------------|
| O       | 65.13                          | 67.67                  |
| Si      | 25.67                          | 27.68                  |
| Al      | 7.07                           | 4.61                   |
| K       | 0.49                           |                        |
| Na      | 0.47                           |                        |
| Ca      | 0.23                           |                        |
| Zr      | 0.21                           |                        |

The content of O and Si elements in the model visualized samples of dendrimer PAS is close to the experimental values. The difference in Al content differs by a factor of 1.5. Perhaps, it can be explained by the discrepancy in the weights of this element in the experimental and theoretical samples. Thus, the choice of oligomer conformer segments to calculate the sizes of dendrimer PAS should be considered reasonable.
One interrupts stage III to obtain the filled AS samples so that the well-proportioned and adequate dendrimer crowns form (see the stage-to-stage scheme of the PAS synthesis). The monomeric precursor-powder nanoparticles are injected in the crowns by mechanochemical mixing with simultaneous ultrasonic treatment. The highly dispersed filler powder has been injected by means of the Emax high-speed ball mill of Retsch company and followed by ultrasonic dispersing. The ultrasonic dispersing of particles is the inclusion of monomeric precursor-powders exhibiting weak van der Waals multiparticle interactions. The monomeric precursor-powders are injected into the voids of the PAS dendritic structures. The molecules of the monomeric precursor-powder penetrate into the dendritic supramolecular structure and increase the interlayer distance. Then the interaction between the layers weakens, and it becomes possible to disperse the nanosized particles under the action of thermal oscillations.

Thus, we have managed to obtain a composite nanostructured material consisting of the dendrimer PAS and monomeric precursor-powder uniformly distributed in it (figure 5).

Figure 5. Microphotograph of PAS with monomeric precursor-powder injected in it (200 nm scale, Philips CM 30 transmission electron microscope).

Figure 5 shows that the PAS dendritic supramolecular structure is densely filled with the monomeric precursor-powder.

The use of the dispersed filler powders obtained by other methods with a layered (scale) structure to inject into the PAS matrix is difficult due to the possibility lack to inject them into the dendrimeric PAS interdomain spaces.

3. Results and discussion

3.1. Ceramic layer printing on an aluminium base by means of 3D aerosol printing

One of the most crucial problems solved in some technological processes and definitely in 3D aerosol printing is to obtain aerosol from dispersed liquids.

The dispersing can be carried out by various methods, the most widespread of which are hydraulic, mechanical, pneumatic, and electrostatic. We have considered the advantages and disadvantages of each method separately in our previous studies.

According to the research results, the most preferable method for us is the pneumatic one that allows working with highly viscous materials without destroying the supramolecular structure of a polymer binder.
We have used the synthesized polyaluminosilicate filled with a highly dispersed filler and the Aerosol Jet 15EX 3D printer of Neotech AMT Company to obtain ceramic layers (figure 6) and the topologies on aluminum bases by 3D aerosol printing with the help of the pneumatic method.

![Figure 6](image6.jpg)

Figure 6. Photographs of metal base samples with dielectric layers applied by 3D aerosol printing.

3.2. Study of the ceramic layers durability on an aluminum base obtained by 3D aerosol printing

A track has been formed on the ceramic coating by means of a high-temperature tribometer with the following specified measurement parameters:

- the track radius is 3.02 mm;
- the applied load is 10 N;
- speed is 5 cm s$^{-1}$;
- the total path traveled is 114 meters.

The durability dependence (the penetration depth of the instrument holder head) on the traveled path has been obtained according to the tribological research results (figure 7). An optical profilometry of the track has been carried out after the tribological research.

![Figure 7](image7.jpg)

Figure 7. Dependence of penetration depth of instrument holder head on traveled path length by sample with ceramic coating on aluminum base.

![Figure 8](image8.jpg)

Figure 8. Track surface 3D image of sample with ceramic coating on aluminum base after tribometric research.

Figures 7 and 8 show that the coating abrasion along the track occurs evenly and without delamination that has a positive effect on the surface treatment of the coatings formed from filled dendrimer PAS in end products and microelectronic devices.
4. Conclusion
The polyaluminosilicate of dendrimer morphology has been synthesized during the research. The most probable conformers to form the dendrimer PAS have been determined by the quantum-chemical assessment of the thermodynamically possible mechanisms to form the populations of short-chain aluminosilicates. The viscometric measurements allowed us to confirm the quantum-chemical calculations and modify the mechanism to obtain the dendrimer PAS.

The synthesis method for the monomeric precursor-powder, the structure and morphology of which allowed obtaining a PAS close-packed polymer supramolecular structure, has been developed to obtain the filled polyaluminosilicates used as materials for 3D aerosol printing. The ceramic dielectric layers with high consumer properties have been obtained with the use of the obtained materials by means of 3D aerosol printing.

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