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Nano-Scaled Ordering in Highly Branched Regular Polymer Structures

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SUMMARY: General features of the structural moieties spatial arrangement were studied by a number of experimental techniques for a representative set of a novel class of dendritic macromolecules: regular polyorganosiloxane dendrimers, polyallylcarbosilane dendrimers with functional groups, polyallylcarbosilane hyperbranched macromolecules, hyperbranched polyethoxysiloxane macromolecules on the way of their transformation towards molecular form of silica, hyperbranched structures based on the products of hydrolysis of $Ti(OBu)_4$ and prepared by a sol-gel method. Dendrimers in solution seemed like ball-shaped uniform particles with the averaged volume density close to their bulk density, whereas hyperbranched macromolecules had much less value of the averaged density. A rather general multilevel structural hierarchy was revealed and justified for the studied hyperbranched macromolecules of dendritic structure, namely: an ultra-dispersed subparticle - a fractal cluster - a single fractal "macromolecule - particle". The peculiarities of a spatial arrangement of the highly branched regular and irregular dendritic macromolecules were tightly related with the results of the molecular dynamic experiments and with the experimental spectra of their molecular mobility. The comparison was made with the data obtained for dendritic macromolecules of other than studied chemical structures and published elsewhere.

Introduction

Macromolecular architecture is an attractive topic for investigations as the search for new polymeric materials with well-defined properties. Many research groups are now focusing their interests on dendritic (treelike, highly branched) macromolecules, i.e., regular dendrimers and less regular hyperbranched polymers based on AB_n-monomers. The extremely high degree of branching and no interchain entangling make dendritic polymers very perspective for the new areas of host-guest and supramolecular chemistry. A number of comprehensive reviews exist that detail the synthesis of these interesting molecular systems[1-14]. At the same time, many of the potential applications for dendritic polymers are directly

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related to the organization and distribution of internal segment densities, the location of terminal end groups, the possibility of reduced density at the core of dendritic macromolecules, the shape of macromolecules and their intermolecular interactions. However, only a restricted number of direct experimental results have been published till now on internal structures and ordering of dendritic macromolecules[15-27].

The recent state of internal dendritic structures understanding remains to be contradictory. For example, there is no coincidence for the prediction[3] about reduced density at the core of dendritic macromolecule, even for regular dendrimer structures. Some results[1,28,29] that have been primarily supported by various computer simulations predict and reveal such a reduction and inner hole or cavities existence inside dendrimer structures, while others[30-33] demonstrate uniform and dense internal dendrimer structures (Fig. 1).

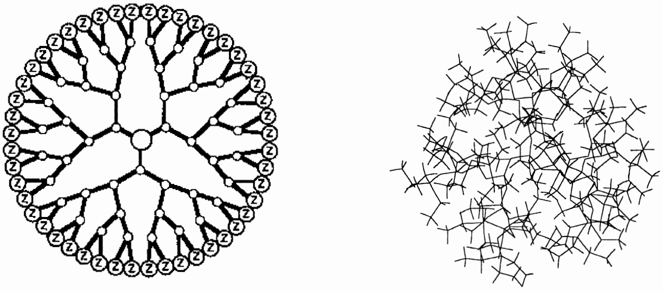

Fig. 1: Planar schematic showing predicted[3] reduced density at the core of dendrimer (left) and spatial skeleton model of dendrimer (right) equilibrated with the experimental results[17].

It is clear that more reliable experimental information should be involved into consideration to build the whole picture of internal dendritic structures correctly. This work will not attempt to review the large number of structural investigations on dendritic macromolecules that have been performed over the past decade. Instead, it addresses some of the moot points in dendrimer research. A comparison will then be made with a number of less regular hyperbranched polymers that retain both a globular shape and a high end-group functionality as regular dendrimers, but have less spatial regularity.

Nano-Scaled Ordering in Regular Dendrimers

The consideration of dimensional hierarchy in life and polymer science shows[3)] that dendrimers occupy a very intrigue alcove as to their dimensions and relative possible applications, namely nanoscopic level. Synthetic nano-scaled macromolecules are very close in size to biological macromolecules. Therefore, the virgin lands exist for mimicry experiments. Dendrimers reveal a great excess of terminal functional groups due to their very specific spatial architecture and the principles of „functional adjusting" and „nano-reactors" can be performed successively in this case. It is why the adequate understanding of the nanoscopic highly branched regular structures seems to be very important for research and development.

Many examples[1-14)] are known for the successive synthesis of dendrimers having various chemical structures. Nevertheless, the experimental methods, being involved into structural investigations, faced with many problems while studding dendritic nano-scaled objects. The main reason is the intermediate between liquid and crystalline range of ordering that is typical for dendrimers and hard to detect.

For example, the simple consideration[3)] shows undoubtedly that dendrimers should have considerable constrictions in the surface area per terminal group and, as a consequence, a great deal of accessible internal surface area in a solvent-filled intramolecular free volume, which may consists of something like internal cavities or channels. The experiments with encapsulation of the guest molecules[34)] and polyelectrolyte behaviour[35)] inside dendrimers proved the prediction mentioned above.

From the other side, the experimental investigations[15-27)] of the internal structure of dendritic macromolecules with SANS and SAXS methods showed the dendrimers in solutions seemed to be like ball-shaped monodisperse particles with a uniform inner density distribution and the averaged volume density close to their bulk density.

The list of similar contradictions may be rather long. Nevertheless, it seems to be a reflection of the recent stage of the problem only. In particular, it is obvious now[33)] that the electrostatic interactions may play an important role in establishing of the dendrimer structures among other things and this situation should be investigated more exactly. It can be stated also that the dendrimers of various chemical structures should have the differences in the structures and properties and that sweeping generalization may be not correct. We need more and more reliable information to build the true whole picture of the structure of dendrimers.

Besides the spatial ordering, the intramolecular and intermolecular interactions have a great meaning in dendrimer structural investigations. Many questions of practical importance should be answered there and a real dynamics of dendrimers and possible mutual interpenetrating are only two among others.

Recent results36,37) on the carbosilane dendrimers with shielded hydroxyl groups at the silicon atoms gave a possibility to distinguish between the outer shell of dendrimer opened for intermolecular interactions and its inner region with the functional groups inaccessible for such kind of the interactions. The similar findings may be crucial for some practical applications of dendrimers like heterogeneous catalysts and should be solved for the dendrimers of various chemical structures separately.

The investigations38-41) of the molecular mobility in the dendrimers of various chemical structure revealed several features specific for the dendrimers only. In general, the relaxation spectra of the dendrimers were found to be similar with the relaxation spectra of typical high molecular weight polymers. The translation diffusion of a dendrimer as a whole could be distinguished also in addition to the normal modes of relaxation (Fig. 2) that was predicted earlier42).

There are a wide number of possible applications declared for dendrimers (see, for example, the comprehensive review43)). Nevertheless, some of the applications should be revised as to their efficiency. Let us consider the simplest characteristic of the polymer with the functional groups to be exploited, namely so-called the „equivalent molecular weight" (EW). The value of EW is equal to the molecular weight of the polymer divided by the number of the functional groups, presenting the efficiency of the functional groups inside the polymer structure. Fig. 3 presents such an estimation for the three types of the popular synthetic schemes: poly(propylene imine) dendrimers44,45), poly(amido amine) dendrimers46) and poly(methylsiloxane) dendrimers47).

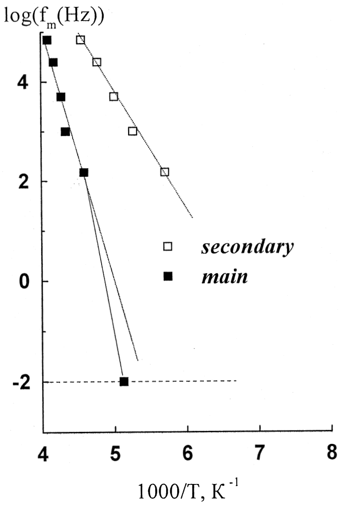

Fig. 2: Temperature dependence of the relaxation processes in poly(allylcrbosilane) dendrimer of the fourth generation[41)]: ■, α process with Vogel-Fulcher fit; □, β relaxation with Arrhenius fit. The date at $\log(f_m) = -2$ corresponds to the radiothermoluminescence method and reveals the translation diffusion of a dendrimer as a whole.

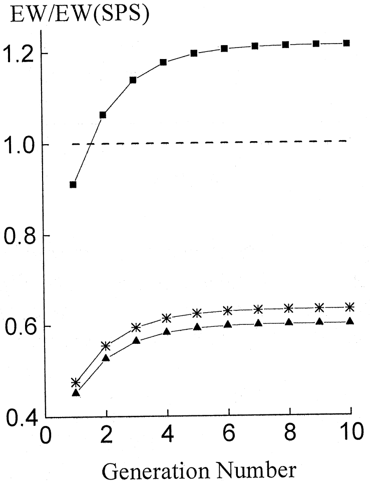

Fig. 3: The relative equivalent molecular weights for the dendrimers of various chemical structure: ■ - poly(amido amine) dendrimers[46)]; ▲ - poly(propylene imine) dendrimers[44,45)]; ✳ - poly(methylsiloxane) dendrimers[47)]. Dotted line at EW = 1 corresponds to poly(styrenesulfonic acid) (SPS).

The comparison was made with respect to poly(styrenesulfonic acid) (SPS) which could be used as the standard reference functional polymer (ion-exchange resin).

Fig. 3 shows that there are no bright advantages of the dendrimers while comparing with common polymers with the regular arrangement of the functional pendant groups. It is why the several applications for the dendrimers may be not so exciting as declared. Of course, each of the cases should be checked and verified separately.

The spatial ordering and properties of dendrimers based on their regularly branched structure are unique features of these globular-like macromolecules. However, as was yet stated before8), the price that has to be paid for these special properties is one of accessibility. At the same time, there is another one branch of polymer chemistry laying very close with the chemistry of dendrimers synthesis and more attractive from the viewpoint of the practical applications, namely hyperbranched polymers. Hyperbranched polymers are easily obtained by a number of one pot procedures and their synthesis may be arranged like a relatively cheep process. The hyperbranched polymers mimic to some extent the dendrimers, possessing own distinctive features.

Nano-Scaled Ordering in Hyperbranched Macromolecules

P.J.Flory, in 195248), described the concept of the hyperbranched macromolecule synthesis, starting with the new class of branched polymers. As proposed, the concept stated that: „Highly branched polymer molecules may be synthesized without incidence of gelation through the use of a monomer having one functional group (A) of one kind and two or more of another (B) capable of reacting with the former...Such polymerization offer unique advantages for the preparation of highly branched polymers suitable for investigations on the influence of non-linearity on physical properties."

Flory presented the hyperbranched polymer from a theoretical point of view, describing the intermolecular condensation of AB_n-monomers. The first successive synthesis of the hyperbranched polymer was reported by Kim and Webster49), starting the intensive research work in this field8,9). The hyperbranched polymer structures are important because of the attractive combination of their features8,9): (a) noncrystalline and nonentangled structure of high molecular weight; (b) possible variation in branching degree; (c) possible keeping of particle-like form; (d) good solubility and decreased melt viscosity; (e) wide area of possible applications (thermoset resins, toughening agents, coatings, etc.); (f) cheap synthesis.

It was demonstrated[22] that the hyperbranched macromolecules in solution were sufficiently dense and had particle-like form, despite having an inhomogeneous internal spatial structure. The value of the averaged volume density of the hyperbranched macromolecules was found[22] to be remarkably lower than of the dendrimers and remarkably higher than of the linear polymer of the same chemical structure. A rather general multilevel structural hierarchy was revealed and justified for the studied hyperbranched macromolecules of different chemical structure[22,50-52]. As an example Fig. 4 shows SAXS curves for the hyperbranched macromolecules in solutions with a very striking similarity in the spatial ordering, irrespective of their exact chemical structure.

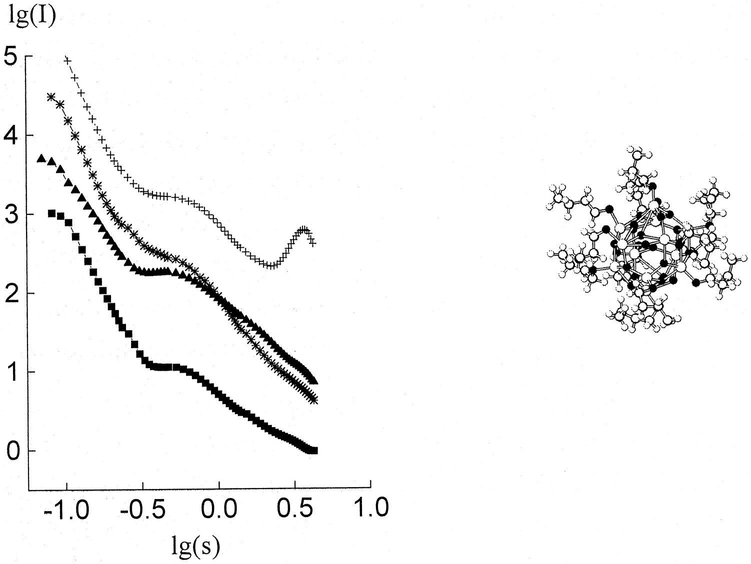

Fig. 4: SAXS curves for the hyperbranched macromolecules of different chemical structure (left) and a typical „brick" or an ultra-dispersed subparticle (right) for the rather complex spatial construction of the hyperbranched macromolecule, derived and adjusted from the experimental data[52]. ■ - the product of hydrolysis of $Ti(OBu)_4$[52] („two-levels" conditions); ▲ - poly(ethoxysiloxane)[51]; ✳ - poly(allylcarbosilane)[22,50]; ✚ - the product of hydrolysis of $Ti(OBu)_4$[52] („three-levels" conditions).

The three levels of hierarchy can be distinguished confidently: an ultra-dispersed subparticle - a fractal cluster - a single fractal "macromolecule -particle". It seems that the revealed similarity reflects meeting the demands of Flory conditions[48)] for the reacting monomers to form the hyperbranched polymers. The hyperbranched macromolecules[22,50-52)] were built mainly with the intemediate „substructures" rather than by „random" attachment of the monomers and the relative content of the structural components could be changed upon changing in the polymerization conditions. Thus, the new possibilities were opened to construct the hyperbranched macromolecules by request.

Conclusions

It goes without doubt that there is an impressive success in chemistry of highly branched regular and irregular polymer structures. Nevertheless, more and more reliable data are necessary concerning their spatial structure and properties to satisfy the growing requirements and to throw down a challenge from the industry of the new materials.

Acknowledgments

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