Structure and Dynamics of Dendritic Macromolecules

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Summary: The highly branched regular organosilicon polymer structures (dendrimers) were examined. A number of experimental techniques were used to study the structure and dynamics of dendritic macromolecules in a bulk state as well as in diluted solutions. The reliable quantitative structural and dynamical characteristics, which were obtained within a framework of a complex investigation, arranged a background to resolve several of the contradictions in accounting for the results coming from the various experimental methods and numerical calculations. The explanations were found for: (a) why dendrimers look as penetrable and impenetrable with the solvent at the same time; (b) why dendrimers reveal typical for the linear polymers segmental relaxation spectra and possess a translation diffusion of the whole macromolecule in addition. The small-angle neutron scattering experiments on the dendrimers with the specially labeled terminal groups showed that the terminal groups are concentrated near the periphery of the dendrimer structure.

Keywords: dendrimers; dynamics; neutron scattering; relaxation; structure

Introduction

The specific spatial architecture of dendritic (treelike, highly branched) macromolecules makes them very perspective for the new areas of host-guest and supramolecular chemistry.[1-3] The wide range of the proposed potential applications[1-9] of the dendritic macromolecules is directly related and decisively dependent on their real structure and dynamics. Nevertheless, the recent state of the dendritic structures and dynamics understanding remains to be rather contradictory.[10]

There is an evident impressive success in the chemistry of the highly branched regular and

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irregular structures.[1-17] On the other hand, numerical calculations, molecular dynamics simulations and theoretical approaches[18-24] to the structure of the dendritic macromolecules seem to be less unambiguous, even though rather numerous. It should be recognized,[1,11] that there are important differences between different dendritic structures and that sweeping generalization may be not correct. On the contrary, for the large activity on the dendritic polymer synthesis and structure computations, there are only few experimental studies on dendrimer and hyperbranched macromolecular structures. For such a reason, many findings in simulations have still not been experimentally verified. The following recently calculated results may be very important when assessing the viability of a dendritic structure in a particular application and should be experimentally proven: (a) the density of monomers is rather high at the core of dendritic structure and decreases towards the periphery; (b) the free ends of the dendrimer are distributed throughout the macromolecule with a high degree of chain back-folding for higher generations; (c) the density profile of the dendritic macromolecule is tunable from the dense core to that of the dense shell by changing the outer conditions.

The goal of this work was to collect quantitative structural and dynamical characteristics of the dendritic macromolecules within a framework of a single complex investigation, arranging a background to resolve several of the contradictions in accounting for the results coming from the various experimental methods and numerical calculations.

Regular Dendrimers

The starting point of our investigation was a concept[25,26] of the outer and the inner shell within a dendrimer spatial structure. For the carbosilane dendrimers with the shielded hydroxyl groups at the branching silicon atoms, it was possible to distinguish[25] between the outer shell of the dendrimer opened for the intermolecular interactions and its inner region with the functional groups inaccessible for such kind of the interactions in solution. The mutual interpenetrating of the rather big dendrimers was found in these experiments to be restricted to their thin outer shells only. In this relation, we studied whether or not and to what extent the small molecules of the solvent can penetrate inside the dendrimer structure.

The internal structure of the dendrimers in the diluted solutions was investigated with small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) methods.[27] The SANS measurements were carried out using the YuMO facility at the IBR-2 reactor of the JINR, Dubna. Three generations (G5, G6 and G7) of poly(allylcarbosilane) dendrimers were studied in benzene-d_6, chloroform-d and in the mixtures of bezene/benzene-d_6. Two-dimensional picture of the G5 dendrimer structure is shown schematically in Figure 1 as an example. A form of SANS curve for the G7 sample in benzene-d_6 is illustrated in Figure 2.

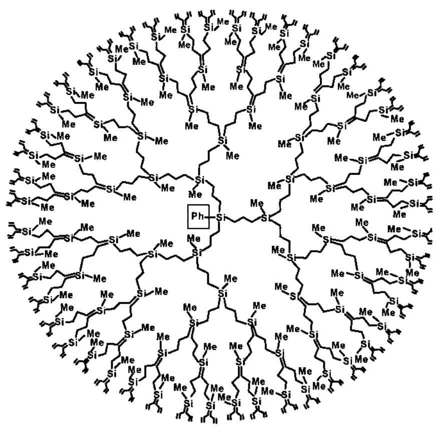


Figure 1. A two dimensional representation of the fifth generation (G5) of the poly(allylcarbosilane) dendrimers. The structure comprises a three-functional core (phenyl-substituted), 94 branching atoms (Si), 96 terminal groups (allyl). M = 11971 Da.

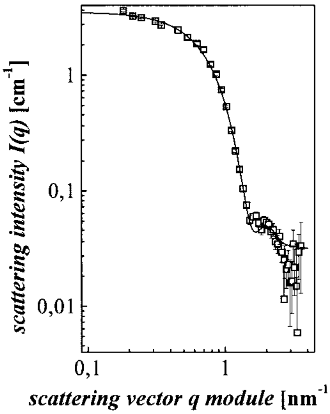


Figure 2. SANS curve of 4 wt.-% solution of the G7 dendrimer in benzene-d_6.

The best fits of the scattering curves for all of the dendrimers (G5 - G7) yielded the uniform spherical globes model for a wide range of the solution concentration and for the different solvents. The model of the uniform ellipsoidal scattering particles gave nearly equal a, b and c values of their axes while fitting the same set of the curves. Thus dendrimers in solutions seem to be uniform globular-like particles (i.e. the same density value for any small part inside the volume restricted by the boundary surface of the scattering particle).

The inner density distribution of dendrimers was checked by the contrast variation method (SANS). Figure 3 represents the radius of gyration values calculated from SANS curves for the G5-G7 dendrimers upon changing of the scattering density of the solvent. Figure 4 gives the variation of a so-called "zero angle scattering intensity" under the same conditions.

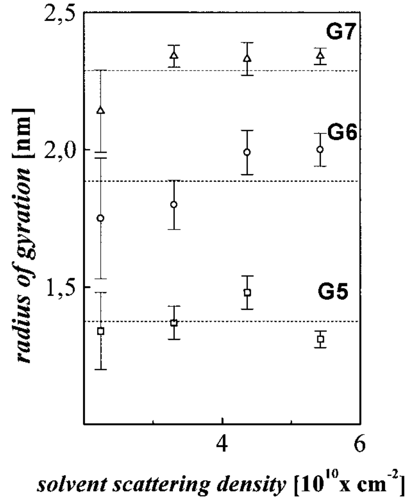


Figure 3. Radius of gyration calculated from SANS curves of 2 wt.-% solutions of the G5-G7 dendrimers in the mixtures of benzene/benzene-d_6.

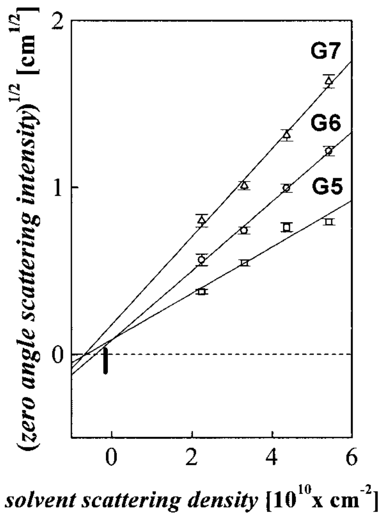


Figure 4. Zero angle scattering intensity experimentally determined from SANS curves of 2 wt.-% solutions of the G5-G7 dendrimers in the mixtures of benzene/benzene-d_6. Vertical dash corresponds to the scattering density of the pure dendrimers in a bulk.

The invariance of the radius of gyration of the dendrimers in Figure 3 gives one additional proof[28] of the uniform density distribution inside the dendrimer structure. The scattering density value of the dendrimers in solution found in Figure 4 from the intersection of the experimental scattering intensity with the zero intensity level upon the contrast variation, being coincident with the scattering density of the dendrimers in a bulk, demonstrates (admit an assumption that there are) no closed inner holes inside the dendrimer structure impenetrable with the solvent. Now the question arises how to equilibrate these data with the numerous findings[29, 30] on a great deal of accessible internal surface area in a solvent-filled intramolecular free volume of a dendrimer.

To solve this contradiction the SANS absolute intensity measurements were performed,[27] allowing direct calculation[28] of the particle (dendrimer) volume V_p in solution, impenetrable with the solvent. The standard procedure[28] was used for the elimination of the interparticle interference effect on the calculated form factor of the dendrimer (Figure 5). The effective volume of the dendrimer $V_{eff} = (4/3)\pi R^3$, where the R-value was calculated from the radius of gyration value, was compared with the V_p value. The V_{eff} value was found[27] to be 30-40 % higher than the V_p value.

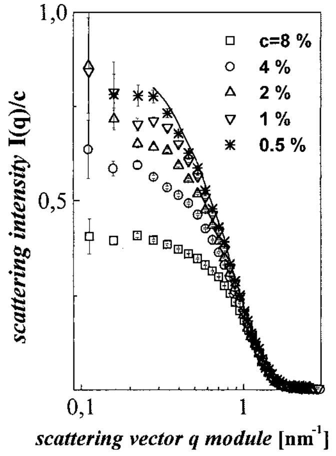
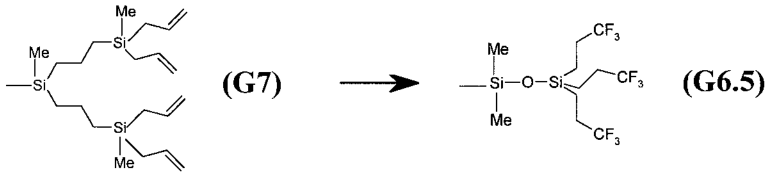


Figure 5. SANS curves of the solutions of the G6 dendrimer in benzene-d_6 at the given concentration c (wt.-%). Solid line represents the form factor of the dendrimer (infinitely diluted solution with c = 0 %).

The obtained results undoubtedly showed the remarkable penetration of the small molecules inside the effective dendrimer volume V_{eff} rather than inside the dendrimer volume V_p. It is why we can speak about the dendrimer to be penetrable and impenetrable with the solvent at the same time.

The location of the terminal groups inside the dendrimer structure was also tested within a framework of the same complex investigation.[27] The modification of the terminal groups for the G7 dendrimer was performed in accordance with the following scheme:



By matching the scattering density of the appropriate solvent (the mixture of toluene/acetone-d_6), it was possible to screen the SANS from the terminal groups of the modified dendrimer G6.5. The residual SANS curve of the G6.5 dendrimer locates just exactly in between the SANS curves of the G6 dendrimer and the G7 one (Figure 6), as well as the appropriate value of the radius of gyration[27]. Thus the near the surface location of the terminal groups was determined inside the dendrimer structure. This finding is consistent with the results published elsewhere.[31]

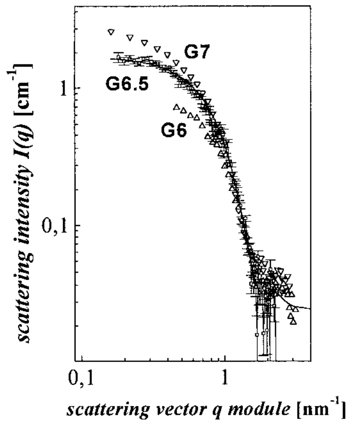


Figure 6. SANS curves of 2 wt.-% solutions of the G6, G6.5 and G7 dendrimers.

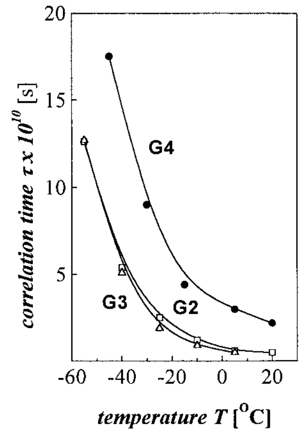


Figure 7. The temperature dependence of the correlation time of the spin probe rotation for the G2, G3 and G4 dendrimers in a bulk state.[33]

The investigations of the molecular mobility[32] revealed the relaxation spectra of the dendrimers to be similar with the relaxation spectra of typical high molecular weight polymers, that may be ascribed to the cooperativity among the dendritic arms.[33,34] The true "polymeric" behavior of the dendrimers can be reached already with their small generation number (G3-G4), as was shown with poly(allylcarbosilane) dendrimers by applying an ESR spin-probe technique (Figure 7).[33] In addition to the normal modes of relaxation, the translation diffusion of a dendrimer could be distinguished also.[32]

Conclusion

The dendrimers, being macromolecules and particles at the same time as to their properties and behavior, possess a number of features specific for the dendrimers only. The dendrimers reveal typical for the linear polymers segmental relaxation spectra and possess a translation diffusion of the whole macromolecule in addition. However, their interaction with the solvents is very specific. They could take up amount of the solvents strictly defined by peculiarities of the dendrimer molecular structure. As to the results of our complex investigation, such properties could be considered the intrinsic characteristics for the poly(allylcarbosilane) dendrimers, which have to be taken into consideration in future design of functional dendrimers for the purpose of specific application.

Acknowledgments

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