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RECOMMENDATION

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Hydrodynamic and molecular homology of dendrimer molecules

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Abstract The questions of the structure, molecular and hydrodynamic homology of hybrid dendrimers molecules are discussed.

Key words Dendrimers · Homology · Molecular hydrodynamic properties

The problems of homology and the place of dendrimer molecules in the fields of polymers and polymer systems are the subject of much interest and discussion [1–3]. Considering the first (or zero) generation of polypropyleneimine dendrimers or polyamidoamine dendrimers as the initial generation, various molecular series can be constructed, for instance, a series of comb-like molecules, one of molecules with regular rings in the main chain, one of star-like molecules with a fixed number of arms having different lengths, and finally a series of dendrimer molecules. In each case, we will probably have different scaling relationships of the size of the hydrodynamic values to the molecular weight but these dependences will have the same starting point. The peculiarities of the denderimer series are the regularity of branching as well as the limiting and transitional character of the range of molecular weights. The series of dendrimers usually consists of five or six generations. Moreover, the first and second generations refer to low molecular weight species while the fifth and the following ones consist of macromolecular compounds. It is noteworthy that, in the kingdom of linear polymers in chains within these ranges of the molecular weights, there are considerable changes in many of the characteristics and/or relationships describing the behavior of linear molecules [4, 5]. Thus, the set of experimental data in the case of dendrimers is always limited. However, molecular hydrodynamics becomes more informative with increases in the molecular weight range. The situation becomes more complex when hybrid dendrimer molecules are studied. The chemical nature of the end groups of hybrid dendrimers differs from that of core and, possibly, the end groups exhibit additional, specific interactions with this core.

The discussion of the homology type of hybrid dendrimer molecules is a subject of current interest. In many published articles it is reported that the intrinsic viscosity of dendrimer molecules, including hybrid dendrimers, is very low and independent of the molecular weight or that this dependence has a small maximum depending on the molecular weight or the number of generations. The hydrodynamic characteristics of glycodendrimers based on polypropyleneimine dendrimers [6, 7] and on polyamidoamine dendrimers [8, 9] have been studied in detail by the methods of molecular hydrodynamics. The following results were obtained. The translational friction data exhibit a single dependence on M on a double logarithmic scale with very high values of linear correlation coefficient. The question is: Can we consider the series of molecules in which the translational friction characteristics correspond to scaling dependences with constant scaling indices as a homologous series of molecules?

It was found also that the translational scaling index is close to the value corresponding to that of rigid impermeable spheres. This means that this value predicts that the intrinsic viscosity is virtually independent of M (if we follow the concept of the equivalence of the molecular size in the phenomena of translational and rotational frictions), as has been observed in experiments. The important conclusion from these data is that translational friction is very sensitive to the molecular weight and the size of dendrimer molecules in contrast to the insensitivity of the intrinsic viscosity values.

When comparing the theoretical calculations with the experimental data, it should be taken into account that the polypropyleneimine dendrimers and polyamidoamine dendrimers are short-chain dendrimers. This means that the distances between the two neighboring branching points are short. (It is possible to call them rigid-chain dendrimers because $L/A < 1$, where L is the contour length of the part chain between the adjacent points of ramification and A is the Kuhn segment length of this chain.) It should be taken into account, as pointed out above [4], that the possible increase in the A value is caused by the interactions between the side chains in one dendron and this electrostatic interaction. This could give $L/A \ll 1$.

Theoretical calculations [10, 11] were carried out for the case of branched chains including regular branched chains and for star-like molecules [10, 12–14] with the Gaussian subchains when $L/A \gg 1$. It is not at all evident that the results obtained for long subchains will be applicable for very short subchains.

The problem of a linear analogue is very important or crucial for this kind of interpretation. In this case a knowledge of the scaling indices of linear analogue is necessary. The problem of the composition and structure of the linear analogue is not trivial in the case of hybrid dendrimer molecules. A copolymer for which the scaling index is not a priori equal to 0.5 in a given region of molecular weights and in an appropriate solvent may be considered as the linear analogue.

Note that the number of arms N in real star-like molecules never exceeds the value of 20 ($N < 20$). This is due to very strong steric hindrances in the core of star molecules. In such a case volume interactions should also be taken into account.

At present, a unique real system that exhibits a similar hydrodynamic behavior is the set of globular proteins. It may be assumed that, in spite of different molecular designs, the dendrimer molecules and globular proteins are hydrodynamicaly analogous structures. This is due to the low entropy values of both class of polymers. At the same time, the possibility of entropy change is different for these two class of molecules. However, the hydrodynamic similarity does not imply structural (architectural) similarity. The regular star model does not represent an improved interpretation for hybrid dendrimer molecules. All the present proposed notation has achieved is to demonstrate that the hydrodynamic behavior of star molecules (with an unrealistic number of branches) is equivalent to the behavior of hard impermeable spheres.

The most suitable model for hybrid dendrimer molecules with long end groups maybe a polymer brush on a changing closed and perhaps permeable surface.

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