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COMMENTS ON THE PAPER

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Apparent polymer homology of lactosylated polyamidoamine dendrimers (comments on "Sedimentation, translational diffusion, and viscosity of lactosylated polyamidoamine dendrimers" by Pavlov GM, Korneeva EV, Roy R, Michailova NA, Ortega PC, Perez MA)

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Abstract Hydrodynamic properties of lactosylated polyamidoamine dendrimers with different generation numbers as presented by G.M. Pavlov and coworkers have been rationalized in terms of structural homology on the basis of the regular star model. This interpretation seems to be more adequate for the experimental data than their treatment in terms of the polymer homology of dendrimer molecules using hard, nondraining (or partly draining) models of the spherical symmetry.

Key words Lactosylated dendrimers · Hydrodynamic properties · Homology

Analysis of experimental data

Recently, hydrodynamic investigations of series of lactosylated polyamidoamine dendrimers (LacPAMAM) in dilute solutions were performed in detail [1]. For the six LacPAMAM generations (numbered 1–6) based on polyamidoamine matrices, the properties have been observed to be unusual for synthetic polymers: the first (1) and the last available generation (6) differ from one another more than 37 times in molecular weight, M, and have the same intrinsic viscosity, $[\eta]$. Simultaneously, the coefficients of diffusion, D, and sedimentation, s_0, show significant changes. In terms of polymer homology, the scaling parameters a and b in relations $[\eta] \sim M^a$, $D \sim M^{-b}$ and, $s_0 \sim M^{1-b}$ were evaluated in the cited article for LacPAMAMs to be $a = 0.05$ and $b = 0.37$, respectively.

In terms of hard, nondraining spheroid models, the results $a \approx 0$ and $b \approx 1/3$ are known to be typical for homologous series of particles where an increase in the dimensions is followed by safety in the form of asymmetry [2]. Particularly, this is true for the hard-sphere model, which is widely used in the study on globular proteins. That is why the molecular properties of dendrimers are often compared, on the one hand, with those of the nondraining or partly draining spherical (spheroid) particles, whose linear dimensions grow in proportion to $M^{1/3}$ [1, 3].

On the other hand, the dendrimer molecules belong undoubtedly to a family of branched chains. The geometric dimensions and the asymmetry of the form of such molecules are lower than those of linear ones with equal molecular weight. Therefore, $[\eta]$ and the translational friction coefficient, $f (f \sim 1/D$, and $f \sim M/s)$, for a branched molecule in solution are lower than those of the linear molecule, $[\eta]_{\text{lin}}$ and f_{lin}, respectively, and the difference in these quantities grows with an increasing number of branches, n. Therefore, the relations $[\eta]/[\eta]_{\text{lin}}$ and f/f_{lin} are widely used as suitable hydrodynamic parameters for evaluation of the degree of branching.

Models and hydrodynamic properties of branched polymers

Let n is the number of branches (subchains) and m and m_0 are the masses of the subchain and the monomer unit, respectively, M is the molecular weight, $M = nm$, and the subscript lin denotes the corresponding characteristic of a linear chain with the same monomer unit chemical structure and molecular weight.

The dendritic matrix of LacPAMAM under discussion looks like a regular branched chain with branches of uniform length and trifunctional branching points. A model series of such chains with various n values forms a line of polymer homologues. The statistical dimensions of the chains with $m/m_0 \gg 1$ are calculated in Refs. [4, 5].

The main symptom (indicator) of this type of homology (mass homology) is the clear proportionality between the molecular weight and the number of the branches. Thus, the M/n relation does not depend here on M. In contrast, for the series of hybrid dendrimers under discussion, the M/n relation is not invariant to M, changing from 484 to 355 on passing from the first to the sixth generation. Hence, hybrid dendrimer molecules of different generations differ from one another in both molecular weight and branching regularity, they do not form polymer homologous series, and the model of a regular branched chain with branches of uniform length is not suitable for the LacPAMAMs.

At the same time, the relative mass of the LacPAMAM molecule per terminal chain changes only slightly with increasing generation number: the actual M/N value (N is the number of terminal chains) increases only to 16% on passing from the first to the last generation. This means that the molecular weight of every next generation increases practically in proportion to the number of terminal chains, and the line of the different LacPAMAM generations forms the series of the star structural homologues. A model of regular stars with equal arms may be employed, and the quantity M/N may be accepted as the mass of the effective star arm. So, the regular star model looks to be more suitable for the hybrid dendrimer molecules than the model of regular branched chains.

For regular stars, the radius of gyration is given [6] by $g_R = (3N - 2)/N^2$, where N is the number of arms. The dependencies of the $[\eta]/[\eta]_{\mathrm{lin}}andf/f_{\mathrm{lin}}$ parameters on N are empirically given [7] for unperturbed stars by

$$[\eta]/[\eta]_{\mathrm{lin}}=\left[(3\mathrm{N}-2)/N^2\right]^{0.58},$$

$$f/f_{\mathrm{lin}} = \left(N^{0.5}\left\{2^{0.5}-1+\left[(2-2^{0.5})/N\right]\right\}\right)^{-1/2} .$$

In the present work, the $[\eta]/[\eta]_{\mathrm{lin}}$ and f/f_{lin} parameters were evaluated for stars with various N numbers and then approximated to N by power functions

$$[\eta]/[\eta]_{\mathrm{lin}} \propto N^{\gamma} \ , \tag{1}$$

$$f/f_{\mathrm{lin}} \propto N^{\varepsilon} \ . \tag{2}$$

The γ and ε values thus obtained are plotted in Fig. 1 against N. The exponent γ decreases obviously from −0.45 to −0.55, and ε decreases slowly from −0.1 to −0.2 with N increasing from 5–100. These functions reflect decreases in rotational and translational friction of the star chains with a continuous decrease in their asphericity.

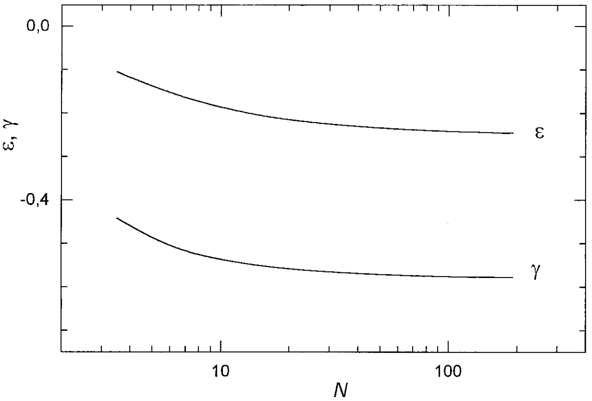

Fig. 1 Parameters γ and ε in Eqs. (1) and (2) against the number of branches, N, calculated for regular stars with equal arms. Details of the calculations are given in the text

There is clear proportionality, $M \propto N$, in the series of model regular stars with increasing numbers of equal arms (main indication of homology of this type), and the molecular-weight scaling of the hydrodynamic parameters is described by the relations

$$[\eta]/[\eta]_{\mathrm{lin}} \propto M^{\gamma} \ , \tag{3}$$

$$f/f_{\mathrm{lin}} \propto M^{\varepsilon} \ . \tag{4}$$

For linear molecules we assume now the Mark–Kuhn equations, $[\eta]_{\mathrm{lin}}= K_\eta M^a$ and $f_{\mathrm{lin}} = K_f M^b$, in which a, b, K_η, and K_f are numerical constants for a given polymer. Then, for series of regular stars, Eqs. (3) and (4) are rewritten as

$$[\eta] \propto M^{\gamma+a} \ , \tag{5}$$

$$f \propto M^{\varepsilon+b} \ . \tag{6}$$

The functions $[\eta]_{\mathrm{lin}} \propto M^{0.5}$ and $f_{\mathrm{lin}} \propto M^{0.5}$ are typical for unperturbed flexible linear chains. So, in flexible limits, we obtain $\gamma + a \approx 0$ and $\varepsilon + b = 0.4 - 0.3$ (or slightly higher values for semiflexible chains), which may be expected for the series of structural homologues. These exponents are very close to those obtained experimentally in the cited article. Namely, weak dependence of $[\eta]$ on M with exponent $\gamma + a = 0.05$ and proportionality $D \propto M^{-0.37}$, yielding $\varepsilon + b = 0.37$ were observed [1].

More quantitative analysis of the experimental data in comparison with theoretical results could be available if we used the exponent a and b values which are more suitable to hydrodynamic properties of the corresponding linear chains in the same solvent. Excluded-volume effects can be taken into account with the procedure described [8] as well as specific extended configurations of arms (end-fixed linear chains) when compared with those of isolated linear chains [9].

The experimental data agree evidently better with the regular star model than with the regular branched chain one. The form and the draining of these molecules depend on the molecular weight/number of arms in the manner usual for structural homologues of this family. Hence, the hydrodynamic size and the form asymmetry of the hybrid dendrimer molecules are determined mainly by the periphery terminal chains, where the main part of the dendritic mass is concentrated.

Molecules of a dendritic matrix with the highest generation number can be supposed to be the most spherical in form (impossibility to prepare the next generation may reflect a compact packing of the external molecule shell, and this shell is likely to be nearly spherical in form). In turn, the dendritic matrix molecules of lower generations look like regular highly branched molecules rather than spherical (or globular) particles. The degree of globulization here is low (dendrimer substance occupies not more than one-third of the macromolecule volume in solution) and is comparable with that observed earlier for highly branched Ficoll molecules [10]. The same conclusions follow from some other experimental studies [11] and theoretical model simulations [12, 13].

The origin of the unusual dynamic properties of a series of dendritic matrix molecules [14] remains a matter of discussion and may be found in very short branches and unique 100% branching of the chain that is unachievable for polymers of other families. For the present time, hyperbranched usual polymers are characterized with 60–80% degree of branching only [15, 16].

Conclusion

Principles of structural homology have been successfully applied here to the interpretation of the hydrodynamic data obtained for different LacPAMAM generations [1]. The experimental results agree well with theories developed for the model of regular stars with equal arms. This agreement was achieved without any limits to draining and form symmetry of the dendrimer molecules. We may conclude that, possessing symptoms of structural homology, hybrid dendrimers of different generations do not form polymer homologous series, meaning the usual type of molecular-weight homology. Their molecules differ from one another not only in molecular weight but also in the branching parameter, without proportionality between these characteristics. Therefore, application of principles of molecular-weight homology to hybrid dendrimers of different generations as well as the comparison with hard particles of spherical symmetry (particularly with globular proteins) seems to have no foundation.

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