Pseudo-Dendrimers

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Dendronized Hyperbranched Macromolecules: Soft Matter with a Novel Type of Segmental Distribution

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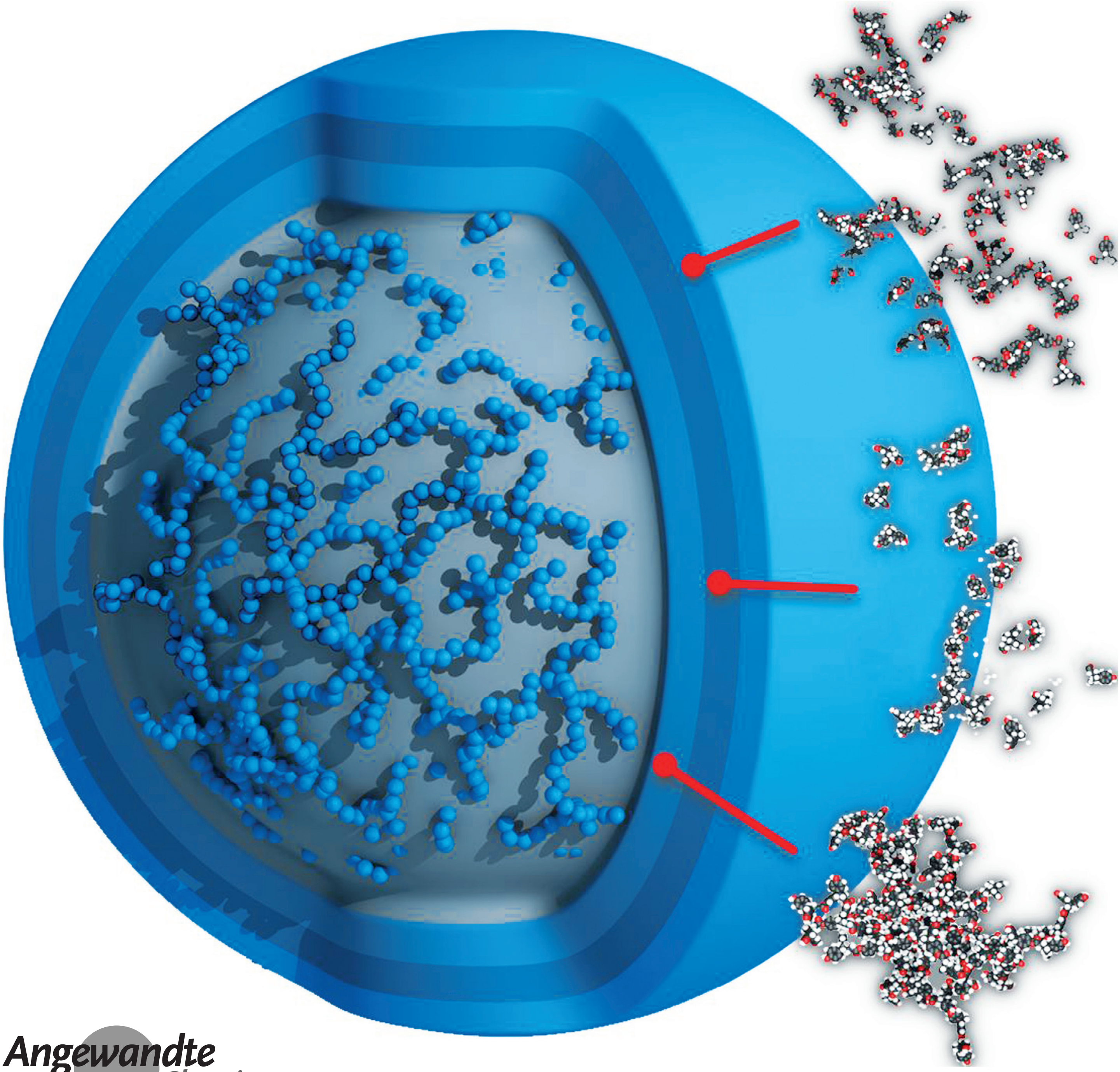
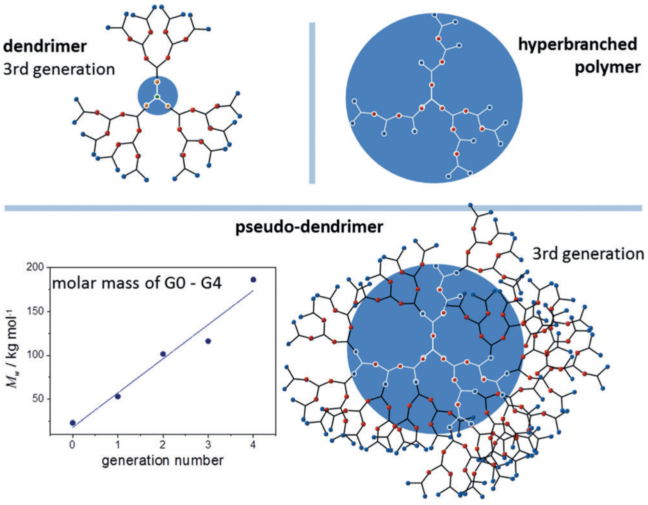


Abstract: *Dendronization of a hyperbranched polyester with different generation dendrons leads to pseudo-dendritic structures. The hyperbranched core is modified by the divergent coupling of protected monomer units to the functional groups. Compared to dendrimers, the synthetic effort is significantly less, but the properties are very close to those of high-generation dendrimers. The number of functional groups, molar mass, and rheology behavior even in the early generation (G1–G4) pseudo-dendrimers strongly resembles the behavior of dendrimers in higher generations (G5–G8). Comparison of the segmental and internal structure with perfect dendrimers is performed using SANS, dynamic light scattering and viscosity analysis, microscopy and molecular dynamics simulation. The interpretation of the results reveals unique structural characteristics arising from lower segmental density of the core, which turns into a soft nano-sphere with a smooth surface even in the first generation.*

Dendrimers are well-defined, unimolecular three-dimensional nanostructures. For more than a decade they have continuously aroused considerable attention in technological applications of biomedical and materials science.[1] Compared to the perfectly constructed dendrimers, hyperbranched (hb) polymers appear like their “ugly cousins”.[2] Hyperbranched polymers have a lower branching degree, fewer functional groups, and lower segmental density, but they have one major advantage—the ease of synthesis. They are readily prepared in a “one-pot”-reaction and are significantly less expensive than dendrimers. In addition, while dendrimers can be prepared only in a limited size owing to complicated synthesis, statistical hyperbranching can lead to extremely high molar masses. Evidently, it would be highly beneficial to have a simple recipe to obtain high segmental density and a large number of functional groups in hb polymers close to those of dendrimers.

The post-modification of hb polymers leading to pseudo-dendrimers was first realized by Frey et al. for polycarbosilanes.[3] Haag et al. expanded the strategy to polyglycerols,[4] and Kakimoto et al. attained complete modification of the free functional end-groups from hyperbranched polyimides.[5] These modifications remained limited to the preparation of pseudo-dendritic structures with only one generation, yet a degree of branching similar to dendrimers was obtained. Multiple-generation pseudo-dendrimers were just recently prepared from hyperbranched aliphatic-aromatic polyesters using post-modification by a divergent dendritic approach.[6] The viscosity of these pseudo-dendrimers follows tendencies similar to those found for dendrimers.[7] The question arose: what is the reason for this similarity? Is it the segmental density distribution of pseudo-dendrimers which resembles those of dendrimers? And if this is the case, could pseudo-dendrimers replace perfectly structured dendrimers, which are at present preferred for special applications, for example, for drug delivery?[8]

To answer this question, we should go one step back to the basic differences in the structures of dendrimers and pseudo-dendrimers. The multistep synthesis of dendrimers yields a 100% degree of branching (Scheme 1), with perfectly branched shells and a number of repeat units which increases exponentially with the generation number. Solely, the terminal units at the highest generation carry the functional groups. In contrast to dendrimers, the functional groups in hyperbranched polymers are no longer positioned only at the outmost shell but they are also found inside the macromolecule. The branching points and the length of the chains between two branching points are irregularly distributed and



Scheme 1. Illustration of a hb polymer and a dendrimer of third generation. Hb polymers from AB_2 monomers have dendritic (no free functionalities, red points), linear (one free B-functionality, blue points), and terminal units (two free B-functionalities) with a degree of branching close to 50%.[9] Modification of the free B-functionalities with AB_2 units will lead to a 100% degree of branching.[11] This leads to large molar mass increase in each next generation (see graph). The blue circles denote the core unit in the dendrimer structure and the core (G0) in the pseudo-dendrimer.

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are defined by random statistics.[9] This situation causes a considerably more open spatial structure and a lower segment density than observed for dendrimers. Scheme 1 depicts the structural differences between hyperbranched polymer, dendrimer, and pseudo-dendrimer in a two-dimensional manner. It is worth noting that the molecular density distribution of dendrimers in fact depends on the rigidity of the monomer structure.[10] Dendrimers are generally characterized by open cavities in the inner part of the molecules and a compact outskirt area which gets denser with the generation number.

Dendrimers and pseudo-dendrimers contain only dendritic and terminal units, that is, every monomer unit is a branching point (except the terminal units). Theoretically, they are both completely branched with 100 % branching degree, but in contrast to dendrimers the pseudo-dendrimers are irregularly branched. Pseudo-dendrimers contain an hb polymer as a core denoted as the zeroth generation (G0). After substitution of all the functional groups by AB_2 units the first generation G1 is obtained. Further modification in the same manner leads stepwise to the next generations G2 to G4.

By this procedure pseudo-dendrimers are obtained with properties similar to those of dendrimers in higher generations (G5–G8) but with less synthetic effort. Even in the first generation the pseudo-dendrimers have high molar masses and an end group number of 100, which increases to 800 in the fourth generation (with a degree of polymerization of around 50 for the hb core). Surprisingly, we observed the characteristic rheology behavior for dendrimers right after the first modification, that is, in G1.[6] These findings show that pseudo-dendrimers could be an interesting alternative to dendrimers in applications where higher generations come into play. In this context the question arises, how similar are the segmental density distributions of both topologies and what is their dependency on the generation number?

Herein we show similarities and differences in the internal structure and the segmental density between pseudo-dendrimers and perfect dendrimers. This comparison is based on the determination of scaling and branching parameters, which are usually expressed by molar mass dependencies. Note that in contrast to the linear increase of the molar mass with the generation number of pseudo-dendrimers (Scheme 1, Supporting Information), dendrimers show an exponential increase. In this study the comparison of the properties of pseudo-dendrimers and dendrimers is performed based on generation number to enable a correlation between synthetic steps and dendron distribution. The successful synthesis and modification of aliphatic-aromatic hb-polyesters has been described elsewhere.[6] Polydispersities $M_w/M_n < 2$ for all the structures enable data comparison and accurate analysis of the scaling properties. Herein, we report on the global features of pseudo-dendrimers of generation G1–G4, that is, the molar mass M_w, radius of gyration R_g, hydrodynamic radius R_h, intrinsic viscosity $[\eta]$,[6] and inter-particle interactions, for example, the second osmotic virial coefficient A_2. Molecular dynamics (MD) simulation of the first three generations gives a complementary view on the shape of the polymers in solution and the density distribution in the molecular structure. Structural information and experimental details are given in the Supporting Information.

The interpretation of the global properties is based on measurements using small-angle neutron scattering (SANS), a scattering technique working at low wavelength suitable for determination of small molecular sizes (Table SI1). Selected SANS-data are shown in Figure SI1.

The radii of gyration R_g and hydrodynamic radii R_h were obtained from SANS and separately performed dynamic light scattering (DLS) measurements. Surprisingly, the radius of gyration of the pseudo-dendrimers decreases with the generation number and only for the last generation G4 is a tendency towards an increase observed (Figure 1). In general, the change of molecular radii is only very weak in view of the marked growth of the molar mass from 53 kg mol^{-1} to 187 kg mol^{-1} for G1 to G4 (Scheme 1). It may be instructive to recall the behavior of flexible linear chains and of hard spheres as the two extremes of conformations. The radius of gyration of these structures increases with the molar mass with $R_g = K M_w^{\nu}$ with $\nu = 0.588$ for linear chains in a good solvent and $\nu = 0.33$ for hard spheres. These exponents correspond to fractal dimensions of 1.70 and 3 for the chains and the spheres, respectively.[13] For dendrimers the radius increases very quickly with the generation number because of the extreme molar mass increase (Figure 1).[12] But for the pseudo-dendrimers the ν parameter is negative for R_g, while the hydrodynamic radius increases with the generation number (Figure 1).

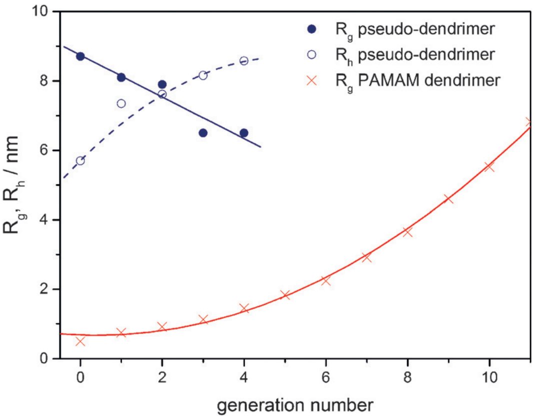


Figure 1. Radii of gyration calculated for 10 generations of a PAMAM dendrimer (crosses)[12] compared to that of the pseudo-dendrimers of 4 generations (filled circles). The corresponding dependence of the hydrodynamic radius R_h is represented by the open circles.

First insight into the apparently contradictory behavior of the pseudo-dendrimer's radii is found when the apparent density is considered. The apparent density can be derived from the radius of gyration and the corresponding molar mass [Eq. (1)].

$$d_{app} = \frac{3}{4\pi N_A} \frac{M_w}{R_g^3} \tag{1}$$

It is helpful to compare these results (Figure 2 A, Table SI2) to those obtained from the hydrodynamic radius shown in Figure 1. As expected, the dendrimers and the

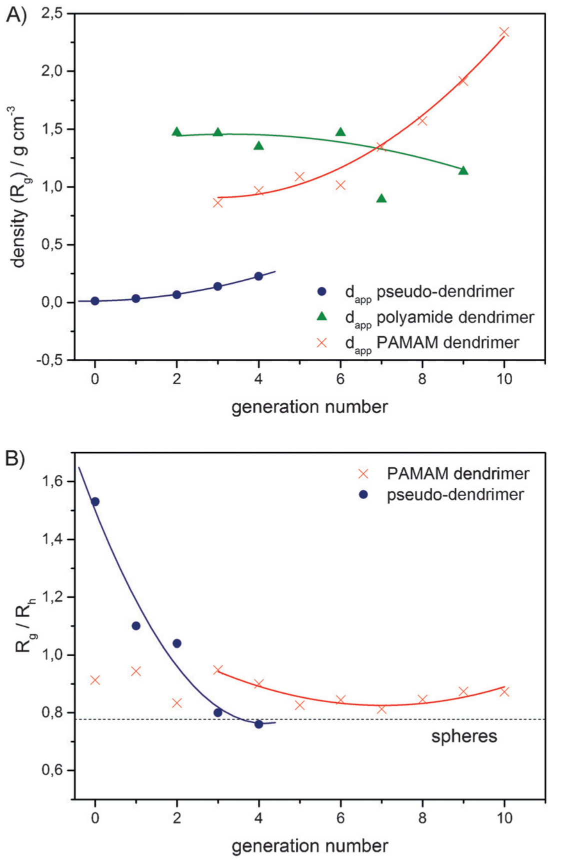


Figure 2. A) Increase of the apparent density with the number of generations for the pseudo-dendrimers from SANS in [D$_6$]THF (circles), for PAMAM dendrimers SAXS in methanol (crosses),[15] and for polyamide dendrimers SAXS in methanol (triangles).[12b,16] B) Behavior of the ρ-parameter of pseudo-dendrimers and of dendrimers of more than four generations. Note that the value of a f-arm star-branched sample, for example, $\rho_{f\text{-arm star}} \rightarrow 1.33$ for $f \gg 3$.[17] The data of R_g for PAMAM dendrimers generation G0–G2 (calculated) are taken from Maiti et al.[12a] for G3–G10 measured with SAXS in methanol by Prosa et al.[15a] and the R_h data by Tomalia et al.[12b]

pseudo-dendrimers exhibit a smooth increase of the overall molecular density with the generation number, pseudo-dendrimers being at much lower densities. This lower density is not necessarily a result of the branching topology but most likely it derives from the rather stiff monomer conformation.[14]

The radii R_g and R_h display a fairly weak change with increasing generations, but notably R_g decreases while R_h increases. The meaning of this opposing behavior becomes evident when the ratio of the two radii is considered [Eq. (2)]

$$\rho = \frac{R_g}{R_h} \qquad (2)$$

The ρ-values are plotted in Figure 2B and compared to those from a series of PAMAM dendrimers. The ρ-parameter is a measure of the branching density and decreases from 1.7 for linear chains, towards lower values with increasing degree of branching, but not below 0.775 for hard spheres. The corresponding values of dendrimers are nearly constant with the generation increase and are close to the values for a hard sphere. This result means that the draining of solvent becomes negligible even in the first generations and a value of $\rho \approx 0.9$ is approached, but even in higher generations the behavior expected for hard spheres ($\rho_{\text{sphere}} = 0.775$) is not reached.[17,18]

In contrast, for pseudo-dendrimers the ρ-parameter strongly decreases with every generation. In the 4th generation it exhibits a very low value, lower than that for dendrimers and close to that of a hard sphere, indicating a particle with a much smoother, denser surface than is apparently present in the flexible dendrimers. The topological changes in the pseudo-dendrimers are reflected by the increasing contrast between the particles and the carbon-film background with the generation number in TEM images of single particles of different generations (Figure 3). This contrast corresponds to the concentration of segments in one particle or, in other words, to the compactness of the macromolecules. MD simulations of generation G0–G2 in THF give an insight into the formation process of the pseudo-dendrimers. Evidently, the less-ordered core structure of G0 has an open segmental arrangement with many linear sections. In the next modification steps leading to G1 and G2, the attached dendrons seem to fill these open spaces within the fringed surface and transform it into a smoother one in the next generation. This tendency is evident in the MD-models in Figure 4, and also confirmed by the radial distribution function and the partial monomer distribution shown in the Supporting Information (Figure SI7). Hence, the decrease of R_g does not necessarily indicate contraction, but likewise it can be caused by a condensed packing of the segments. This result is in agreement with the observed dimensions, because by definition the radius of gyration is smaller than the sphere radius and corresponds to the average distance between the center of mass and the molecular segments. Unlike R_g, the hydrodynamic radius R_h increases because the solvent no longer penetrates the particle but moves around the outer surface defining broader hydrodynamic dimensions of the molecules.

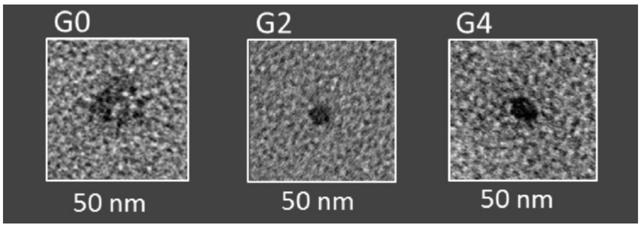


Figure 3. TEM analysis of single particles of generations G0, G2, and G4. Size of the images corresponds to 50 nm. The analysis was performed without any staining so as to evaluate the contrast only on the basis of the particle density. The size of a single particle is not representative for the whole sample, which is characterized by molar mass distribution of 1.7–1.9 in all three examples.[6]

It would be instructive to not only know the behavior but also the physical reason for the difference in the dimensional values. This question was a serious issue in the statistical thermodynamics.[13,19] The profile of segmental distribution could be obtained by the comparison of the two parameters: the draining parameter (Φ) and the interpenetration parameter (Ψ).

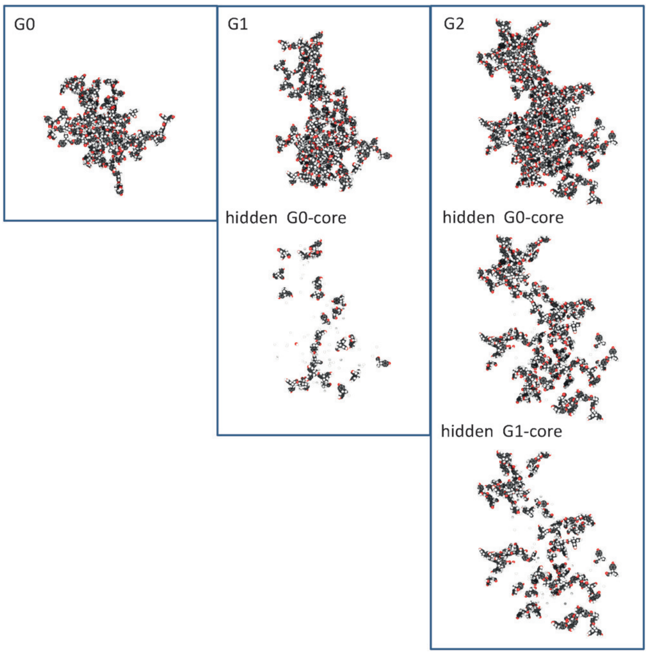
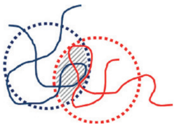


Figure 4. MD simulation of G0, G1, and G2 pseudo-dendrimers with deprotected OH end-groups[6] with degree of polymerization (DP) of 92 of the G0 hb core in THF (solvent molecules are hidden). The Figure shows the full space-filling models as well as the contribution of the post-modification in G1 and G2 to the pseudo-dendrimer formation.

Both, interpenetration of polymer segments and draining of solvent into the polymer are in close relation with the second virial coefficient, A_2 and the intrinsic viscosity, $[\eta]$, respectively. Therefore, information on the equivalent radii, which are calculated from independent intrinsic viscosity measurements (R_η) as well as from the SANS measurements (R_{A2}) could be helpful (see Supporting Information). Linear chains, and even hyperbranched samples, are flexible. They could deform as a result of the osmotic pressure, and the domains of two particles in contact can partially interpenetrate [see schematic representation in Eq. (3)]. Despite tremendous mathematical difficulties agreement was obtained for the behavior of A_2 of open and flexible structures as given by Equation (3)

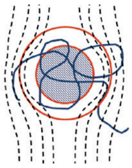
$$A_2M = 4\pi^{3/2}N_A\frac{R_g^3}{M}\Psi^* \qquad \Psi: \qquad (3)$$



with an interpenetration function Ψ which increases with the molar mass but reaches a constant value Ψ^* with the limit of a large number of repeat units in the macromolecule.[19a] The interpenetration factor Ψ^* depends on the particle topology, it is small for deep interpenetration and increases with branching (shallow interpenetration).

A similar effect is observed and theoretically confirmed by the intrinsic viscosity according to Flory and Fox [Eq. (4)] but in contrast to A_2, the magnitude is not determined by interpenetration of the two interacting segment clouds but is caused by the draining effect of the solvent. This situation indicates a somewhat hindered flow of the solvent through the particle as a result of hydrodynamic interactions, which depend on the segmental density. Therefore the draining is impeded more in the center than in the periphery of the particle [see schematic representation in Eq. (4)]. Beyond a certain local density this part of the molecule will be kept swollen but not be drained any longer and the solvent moves around this obstacle like for hard spheres. Thus, the draining factor Φ is determined in a rather complex manner by hydrodynamics and the topology of the particle.

$$[\eta] = \Phi\frac{R_g^3}{M} \qquad \Phi: \qquad (4)$$



The simultaneous information on both parameters, Φ and Ψ, enables clear identification of the type of branching. This relationship corresponds to one of the universal ratios suggested by Oono and Kohmoto[19b,c] for consideration in branching analysis. The universal ratios are 1) the ρ-parameter, already discussed above, 2) the ratio $A_2M/[\eta]$, 3) the static branching (or contraction) factor $g = (R_{g,br}/R_{g,lin})^2$ and 4) the hydrodynamic branching factor $g' = [\eta]_{br}/[\eta]_{lin}$. The calculation of the branching factors shows increasing contraction with the generation number as described and discussed in the Supporting Information.

More interesting is the behavior of the ratio $A_2M/[\eta]$ shown in Figure 5 for the pseudo-dendrimers. The generation dependence of this ratio solely depends on the ratio of Ψ/Φ. The development of these parameters with the generation number is shown in Figure SI3. A smooth but pronounced increase of the draining parameter Φ with the generation number was found, which is in agreement with observations on other branched systems.[20] On the other hand, the spatial interaction parameter Ψ is fairly low for G0 as was also found for other hyperbranched macromolecules,[20a,d] but on stepping from G0 to G1 a sharp increase of Ψ occurs. This effect corresponds to the maximum in Figure 5, after which the ratio shows much greater hydrodynamic hindrance so that Φ increases and the ratio Ψ/Φ decreases again.

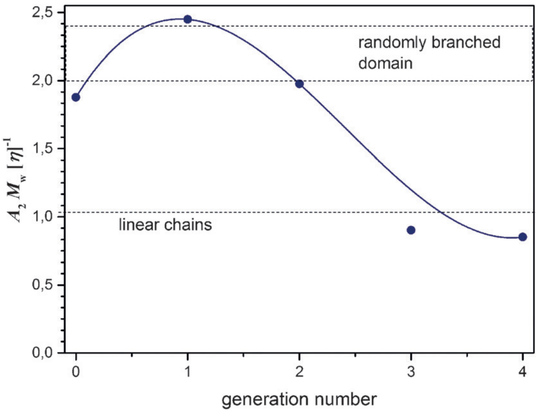


Figure 5. The ratio of interparticle interaction A_2M to the hydrodynamic-viscosity effect $[\eta]$ for different branching generations. The area above 2 is the regime of randomly branched samples so far observed,[20a,d] the dotted line at 1 was predicted by the RG theory[19a] for linear chains in good agreement with experiments.[20b,c,e]

The conclusion which can be drawn is that the attachment of the dense dendritic elements causes a marked, continuous change in the draining effect, while the interpenetration is strongly reduced only for the first AB_2-modification of G0, which leads to a compact pseudo dendritic structure in G1. This fact explains the drop in the viscosity right after the first generation pseudo-dendrimer.

It should be noted that different factors are responsible for the viscosity behavior in dendrimers and in pseudo-dendrimers. The viscosity decreases for dendrimers with more than 4 generations such that finally a nearly constant value can be expected which resembles that of hard spheres. This behavior is a result of a very dense outer area after reaching certain dendron size (after G4).[21] In contrast to them, the high compactness in pseudo-dendrimers is reached in the first generation because of the space filling modification. In the next generations, dendrons as individual, more open arms coupled to this core are formed enabling interpenetration between the molecules (decrease shown in Figure 5), but still maintaining the lower draining of the solvent within the inner dense core conformation. This observation is in agreement with the faster increase of Φ than Ψ in generations G3 and G4.

In conclusion, the detailed analysis of the global structure of pseudo-dendrimers delivers information on the topology development with generation number. The observed transformations give indications on the structural differences to dendrimers. While dendrimers have rather an open structure in the first generations, which gets denser with increasing dendron size, the first generations in pseudo-dendrimers already have a very dense structure. In the higher generations the pseudo-dendrimers still have a very compact core but with some individual open segments at the outskirts. These structures are indicated by hydrodynamic interactions or draining effects, and partially also by hindered segment interpenetration of two interacting particles. The significant increase of the segmental density in the first generation leads to a smooth, compact surface. In contrast to dendrimers, in pseudo-dendrimers no cavities in the inner part are available for, for example, encapsulation of small drugs. Though, their highly functionalized and compact structure is of special interest, for example, as a gene or drug delivery vector by using non-covalent interactions and molecular recognition.

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Keywords: branching parameters · dendrimers · draining parameter · hyperbranched · pseudo-dendrimer

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