Dendron segregation in model dendrimers*

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Monte Carlo calculations on model dendrimers demonstrate that individual branches ('dendrons') of an isolated dendrimer spontaneously demix and are well segregated at equilibrium even when they are chemically identical. This is a result of the particular architecture of this class of macromolecules. It is conjectured that this segregation effect will disappear under high density conditions, e.g. in poor solvents, or at the highest attainable generation number, or in neat fluids of dendrimers. The dendrimers possess fractal self-similarity over a rather narrow scale of lengths with fractal dimensions of the order of 2.4 to 2.8.

(Keywords: dendrimers; segregation; Monte Carlo calculations)

INTRODUCTION

Dendrimers are a new class of macromolecule constructed with a regularly branched, tree-like structure. Syntheses of a number of different dendrimers have been reported by several laboratories[1–6]. Under ideal conditions, the molecular architecture is very regular, as displayed, for example, in *Figure 1*. Let the term 'dendron' designate one of the major subdivisions of the molecule. For example, *Figure 1* displays the division of a dendrimer into three separate dendrons, labelled A, B, and C. Further subdivision is, of course, also possible, and each of the three dendrons divides into two subdendrons, each of which divides into two subsubdendrons, etc.

We have recently reported Monte Carlo calculations on model lattice dendrimers[7]. In this paper, we report an interesting, previously overlooked property of these models. At equilibrium, individual chemically identical dendrons are segregated. This result is somewhat surprising, since it has been generally assumed that separate, chemically equivalent dendrons would intermix.

In the following sections, we present the evidence gathered from the Monte Carlo calculations for dendron segregation, then we qualitatively explain the observed behaviour. We also make several conjectures, as yet unconfirmed, that follow logically from the explanation. Finally, we discuss how some of the conclusions given in the previous publication[7] should be modified in light of this new evidence.

MONTE CARLO EVIDENCE OF DENDRON SEGREGATION

Figures 2 to *4* display projections of dendrimers coloured by dendron, with the projection axis orientation having been optimized to minimize overlap in the two-dimensional projection. These indicate that individual dendrons are segregated. These were drawn from well equilibrated Monte Carlo samples of the indicated generation number g, and are typical of the results obtained generally. Some regions of the diagrams do appear to be intermixed, but this apparent overlap is only a consequence of the projection into two dimensions, a fact which we established by direct observation of computer images.

To establish that the segregation is not due to any bias inherent in the initial configurations, a number of Monte Carlo runs have been performed beginning from thoroughly intermixed conditions. Segregation was observed to occur spontaneously in every case.

Figure 5 displays a time-averaged density projection obtained from a Monte Carlo run of 1.5×10^9 cycles on a dendrimer of generation 7. During the course of this run, the three central bonds attached to the core were

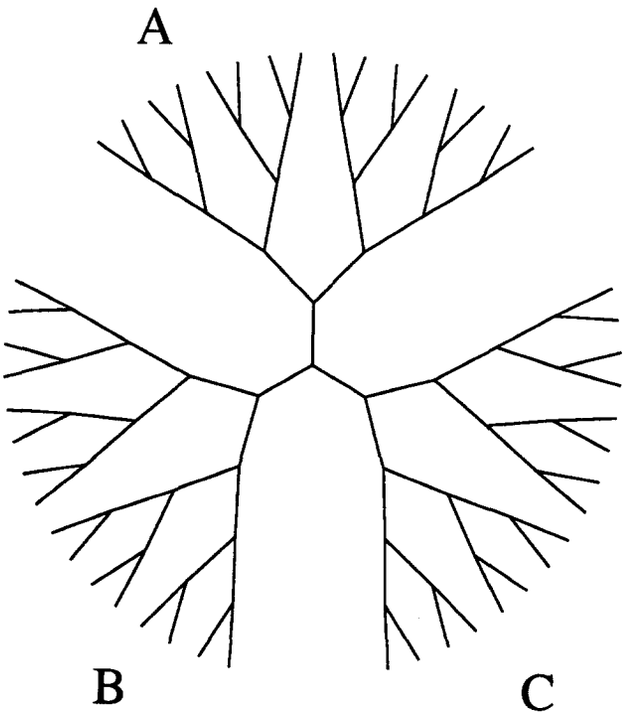

Figure 1 Schematic diagram of dendrimer connectivity, showing subdivisions into 'dendrons' A, B, and C

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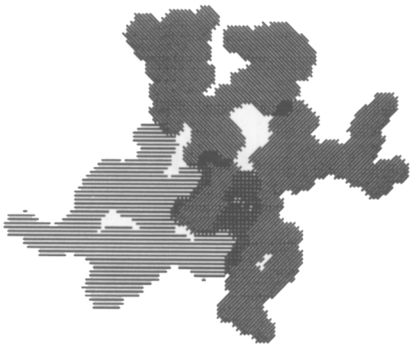

Figure 2 Two-dimensional projection of a $g=3$ dendrimer. To demonstrate dendron segregation, each respective dendron is displayed with a different cross-hatched pattern

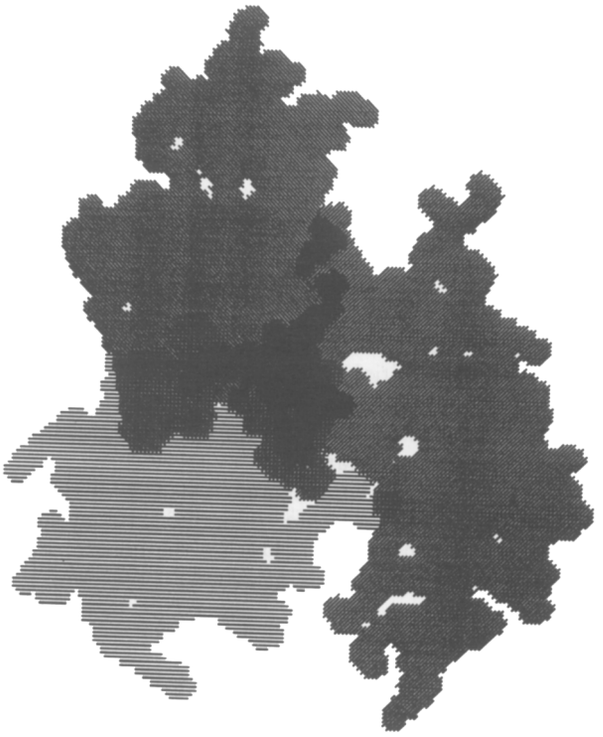

Figure 3 Same as *Figure 2* for a $g=6$ dendrimer

not permitted to move. (The grey-scale level in *Figure 5* is a monotonic function of the number of segments projected onto a given region of the plane throughout the course of the calculation, but to enhance the contrast between regions of low and high density it is not a linear function.) Three regions of high density are clearly discernible, and these correspond to regions of greater probability to find segments belonging to each of the three respective dendrons. Also discernible are the three central spacers. This demonstrates that correlations exist between the orientation of the central core and the spatial distribution of the dendrons. A similar calculation was performed on a dendrimer of generation 3. The resulting plot is not shown, but nevertheless three regions of high density are once again discernible. (In this case, the central spacers could not be discerned, but that is consistent with what we know concerning the extension of the central spacers at various values of the generation number[7].)

Finally, by appropriate colouring of computer images, we are able to observe segregation at the subdendron level in the higher generations. In other words, each dendrimer physically segregates by dendron, and each dendron segregates by subdendron.

EXPLANATION OF OBSERVED BEHAVIOUR

The behaviour described above can be readily explained through the novel architecture of these molecules. In the vicinity of any given segment in dendron A, we can expect to find a rather large density of other segments also belonging to dendron A, solely because of the connectivity of the molecule. To employ an analogy with a family tree, the parents, children, siblings, etc. of the given segment are all required to lie nearby. Let Φ_r denote the local volume fraction of those A segments found in the vicinity of an arbitrary A segment solely on the basis of

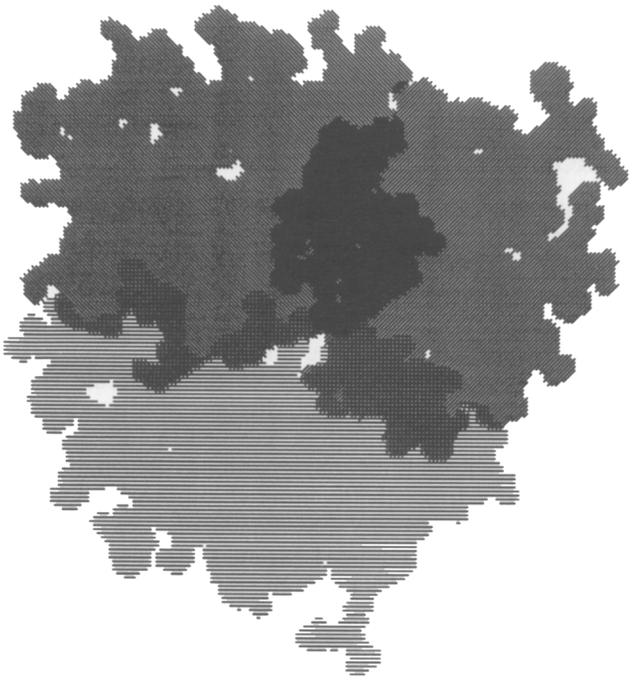

Figure 4 Same as *Figure 2* for a $g=7$ dendrimer

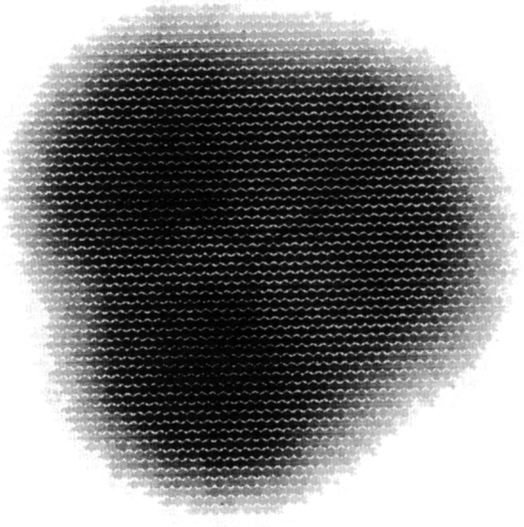

Figure 5 Time-averaged projection of the density of a $g=7$ dendrimer in a reference frame fixed on the central core

close familial relationship, and let Φ_g denote the global volume fraction of the dendrimer. Obviously, if $\Phi_r > \Phi_g$, there is no reason to expect to find any B segments in the vicinity of A segments; A segments are already crowded by their own close relatives and there is plenty of room for B segments elsewhere. Although we have not made any direct computations of the quantities Φ_r and Φ_g for direct comparison, there is little room to doubt that the condition $\Phi_r > \Phi_g$ accounts for this behaviour.

Another obvious consequence is that the dendrimer can be expected to be inhomogeneous. If Φ_l denotes the position-dependent local density in the vicinity of segment A, then obviously $\Phi_l > \Phi_r > \Phi_g$. If there are regions where the local density exceeds the global density, then there must also be regions where the local density falls below the global density. Of course, such inhomogeneities are obvious in *Figure 5*.

CONJECTURES

Two untested conjectures result from this observation. These conjectures will be tested shortly by Monte Carlo calculation.

The first conjecture is that segregation effects of some degree can be expected at the subdendron level, the subsubdendron level, etc. for at least the first few subdivisions. Suppose that dendron A consists of subdendrons A1, A2, etc. and that subdendron A1 consists of subsubdendrons A1a, A1b, etc. Furthermore, just as Φ_g represents the volume fraction of segments defined globally throughout the molecule, we let Φ'_g denote the volume fraction defined globally throughout the dendron A, and Φ''_g the volume fraction defined globally throughout dendron A1, etc. Obviously, we can expect $\Phi_g < \Phi'_g < \Phi''_g < \Phi'''_g \ldots$. This implies that segregation will be observed starting from the highest subdivision and continuing down to that level of subdivision for which $\Phi'''_g \ldots \approx \Phi_r$. Clearly the strength of the segregation will depend on the differences $\Phi_g - \Phi_r$, $\Phi'_g - \Phi_r$, $\Phi''_g - \Phi_r$, etc., so that we can expect the strongest segregation effects at the highest, i.e. dendron, level, and that segregation effects become less pronounced at each level of subdivision until finally, at some level, the respective subunits are effectively miscible. As mentioned above, such lower-level segregation has already been observed in the Monte Carlo calculations at the level of subdendrons.

The second conjecture is that immiscibility effects will disappear whenever Φ_g becomes large. Therefore, we expect miscible dendrons either in poor solvents or in neat fluids. Miscibility should also occur in the terminal generation, although perhaps not universally. This is because Φ_g of a perfectly branched dendrimer in its terminal generation can be anywhere between approximately 0.5 and 1.

REVISION OF PREVIOUS CONCLUSIONS

The results reported here are completely consistent with the results presented previously[7], since both were observed on entirely the same model. However, some of the results given previously were interpreted assuming spherical symmetry, and it becomes necessary to revise some of those interpretations.

In ref. 7, we displayed plots of radial density as a function of distance from the core. These plots exhibit relative minima at intermediate distances from the core, which would imply, if one were assuming spherical symmetry, that these molecules are partially hollow spheres. However, the relative minima in these plots obviously also support the newer interpretation, which is that the molecules are inhomogeneous.

In ref. 7, we presented relative values of the principal moments of inertia of the molecule. (Other authors have also computed average moments of inertia for model dendrimers[8].) The three principal moments of inertia tend to converge as the generation number increases, and this convergence has been taken as evidence that in the higher generations the dendrimers have spherical symmetry. But obviously, an object such as the structure shown in *Figure 5* is sufficiently uniform that its moments of inertia are all nearly equal.

Finally, it should be noted that the segregation discussed here is not inconsistent with the earlier finding that terminal groups are dispersed throughout the molecule. Only in the ensemble average are the respective, segregated subdivisions expected to lie all the same distance from the core. In any instantaneous sample, some subdivisions, along with their attached end-groups, lie near the core, while others lie near the boundary. Therefore, as reported earlier, end-groups are dispersed throughout the molecule.

FRACTAL DIMENSIONS

The hierarchical structure discussed here suggests the possibility of fractal self-similarity. *Figure 6* displays curves constructed to examine this possibility. About every lattice site occupied by the dendrimer construct a sphere of radius R; let $M(R)$ represent the average number of occupied sites in the interior of these spheres. If the object is self-similar, we expect traces of $\log M$ against $\log R$ to be linear with a slope equal to the fractal dimension. These curves are indeed quite linear, although

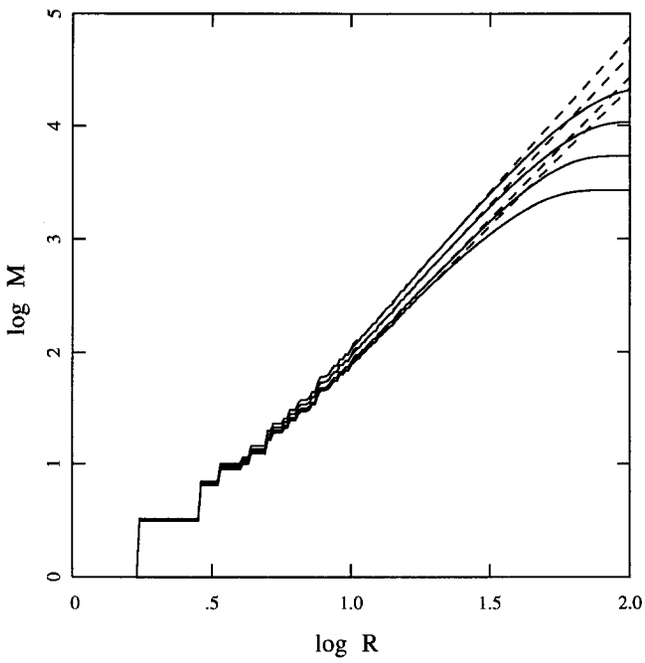

Figure 6 Test for fractal self-similarity on dendrimers of 6, 7, 8, and 9 generations. The dashed lines show the linear extrapolations used to estimate fractal dimensions. The complex structure at small R is a consequence of the embedding lattice

only over a rather narrow range of R values (less than one order of magnitude). The associated fractal dimensions are estimated to be 2.45, 2.52, 2.65, and 2.76 in dendrimers of 6, 7, 8, and 9 generations, respectively. We conclude that these objects may be viewed as possessing a fractal dimension and a fractal self-similarity. However, this self-similarity only extends over a narrow scale of lengths.

CONCLUSIONS

1. Monte Carlo calculations on model dendrimers indicate that separate dendrons of isolated dendrimers are physically segregated. This segregation has been observed at all generation numbers considered ($g = 2$–9), has been observed to occur spontaneously in calculations initiated from intermixed conditions, and has also been observed directly to occur at the level of subdendrons.
2. The segregation is a consequence of the molecular architecture: individual segments are already significantly crowded by 'close relatives', and there is no room nearby for 'distant cousins'.
3. Two untested conjectures can be made. First, the dendrons should intermix under conditions of high density, for example in poor solvents or at the terminal generation. Second, similar segregation effects occur at the subdendron, subsubdendron, etc. levels.
4. The resulting hierarchical organization produces fractal self-similarity, although only over a rather narrow length scale, with fractal dimensions in the range 2.4 to 2.8 for the dendrimers sampled in this study.

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