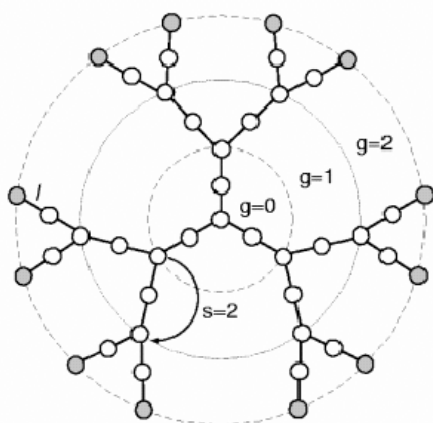


Structure and Flow Properties of Polymeric Dendrimers

Aims and Background: Polymers are long-chain molecules which are ubiquitous in everyday life. As DNA and proteins they perform crucial roles in all biological processes. As plastics they are essential materials for countless industries. Their utility and fascinating behaviour has meant they have long been of interest to physicists and engineers. Thus, at least some of the basic properties of the simplest polymers are well-understood. For instance, we have very good scaling relations for the overall size of simple polymers under different solvent conditions. In particular, one special kind of polymer, the linear, fully-flexible, homopolymer, which consists of many chemically identical monomers connected in a line, has been much-studied. However, most polymers do not fit into this class at all. There are at least three ways in which dramatic differences can be introduced. These are: (a) to introduce non-trivial architecture, so that instead of a linear chain one has a branched chain, a star or a comb, (b) to use more than one kind of monomer (or chemical species) in the polymer so that instead of a homopolymer one has a copolymer. The most common example of these are proteins for which the amino acids are the monomers, (c) to introduce monomers with some stiffness, leading to a semiflexible polymer, the most notable example being DNA.

Combinations of these lead of course to a very wide variety of different polymer types, with equally different physical properties. Indeed it is the possibility of making polymers with the different attributes listed above that makes polymers such useful materials. This proposal aims to look at one particularly important class, the dendrimers. They consist of a regular arrangement of chains branching out from a core, as shown schematically in Fig. 1. These molecules



*Figure 1: A schematic of a dendrimer with functionality $f = 3$, showing the generation number g , and the spacer length s . The terminal groups are shown darker than the other monomers. Taken from *Macromolecules*, 37, p 3049, 2004.*

are interesting from both their fascinating physics and their applications as well-controlled nano-materials [1]. From a fundamental point of view they can be made with almost perfect monodispersity, meaning that each molecule has exactly the same molecular weight. From the experimental point of view they have the advantage, in some cases of being commercially available, bypassing the need for laboratory synthesis. Many applications to medicine have been noted. Moreover since they can be made the same size as a biomolecule, they can be designed to mimic such molecules. They are also model soft materials since they can be made to span the region from hard-sphere colloids to linear high molecular weight polymers. The large number of terminal groups also leads to many applications involving adsorption and self-assembly.

Current understanding of dendrimers is limited to two very small areas. On the one hand we know some things about the structure of simple homopolymer dendrimers (i.e. dendrimers composed of one type of monomer or chemical species). On the other we know a little about how they behave for very simple weak flows. However, there are vast gaps in our knowledge and indeed whole areas which have been unexplored. The aim of our research is to initiate a research program to target these areas, motivated both by fundamental

physical interest and applications. In brief:

- (1) To study and predict the structure of non-trivial dendrimers, i.e. ones composed of more than one type of monomer (copolymer dendrimers), dendrimers involving semi-rigid chains, and dendrimers with modified architecture.
- (2) To understand the rheology (flow properties) of dendrimers, both of the simplest and more complicated kind.

Research Plan: In order to understand dendrimers we need to introduce three simple definitions (figure 1). The generation g , labels which shell number we are at. The functionality, f , labels the number of chains branching out from each branching monomer. The case of $f = 3$ is typical and is shown in the figure. The spacer length, s , labels how long each linear chain which composes the dendrimer is. The figure shows $s = 2$, although s can easily be as large as one desires, up to about a million. Part of the interest in dendrimers is that one can vary s , g , and f along with the kinds of monomers used to produce a very rich variety of structures with very different material properties.

Beyond Homopolymer Dendrimers: There exist several studies of the structure of homopolymer dendrimers where the monomers are all of the same type and where the monomers are fully-flexible. The important upshot of these studies has been that the terminal groups of the dendrimer are actually located throughout the structure i.e. they often loop back and are not located just on the outside [2]. This result implies that a

dendrimer is not a ball with a hollow in the middle and a hard shell, but in fact has a hard core and a soft exterior. This has large implications. In particular they have been strongly pushed as drug-delivery molecules, with the drug being contained in a hollow shell. It thus would be of great importance if one could construct a dendrimer with this hollow shell structure. In this proposal two ways of doing this will be explored through simulations. One is to use stiff semiflexible monomer sequences which are difficult to bend. This helps to hinder the looping back of chains and will produce a hedgehog dendrimer with a hollow structure and with the terminal groups residing preferentially on the outside of the structure. The second method is to use two kinds of monomers A and B that are immiscible in each other. If each generation is made from A and B chains alternating then there will be little looping back for enthalpic reasons—the chains do not wish to mix. The major aim is to study these two kinds of systems to see to what extent qualitative predictions hold true.

Dendrimer Rheology: Examining the rheological (flow) behaviour of dendrimers in solution is a very powerful tool for exploring the relationship between molecular structure and macroscopic behaviour. In our research, we aim to study by means of simulation and theory, the influence that a model dendrimer's particular architecture has on its flow properties when in solution. The exciting recent results of Asteriadi et al. [3] have shown that it is possible to produce complex materials with behaviour and properties exhibiting both polymeric and colloidal features. By altering the spacer length s between 3 and 134 in well-defined dendritically branched polystyrene solutions, they show that the scaling of viscosity with concentration can be made to span the entire range of behaviour between these two limits. To date, there appear to be no theoretical descriptions of this dependence of the viscosity on concentration. Indeed, the description of concentration effects in linear polymer-solvent systems within the framework of exact Brownian dynamics simulations has only recently been attempted [4]. The main stumbling block so far has been the significant increase in CPU time in comparison to dilute solutions due to the presence of inter-molecular interactions. Recently, however, novel simulation algorithms for concentrated colloidal suspensions have been developed that lead to a significant reduction in CPU time [5]. These advances will be incorporated into the dendrimer solution simulation algorithms that will be developed under this research program, enabling the exploration of the dependence of rheological properties on concentration.

The approach used in this research is a combination of analytic theory, and detailed Brownian Dynamics simulation. Several simulation studies in the past decade or so have shown that the well established methods of polymer physics are perfectly suited to the description of dendrimers in solution [2]. Basically, once the fundamental difference in the molecular architecture is taken into account, the *microscopic* physics that governs the behaviour of dendrimers is identical to that which governs the behaviour of linear polymers. Our group has been a vital participant in recent theoretical developments in the description of the rheological behaviour of dilute solutions of linear polymers. This expertise will be brought to bear very fruitfully on the problem of the rheology of dendrimer solutions.

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