

1. Introduction

Precise control of the primary structure and the segmental interaction of natural macromolecules enable them to adopt peculiar tertiary structures, and rendering them to perform various biological processes. In contrast, the introduction of the secondary bonding in synthetic polymers typically leads to the formation of entangled structures and precipitation. So far, the introduction of dense and multiple branching provides the only synthetic approach toward polymers, which do not interpenetrate each other but interact via their surfaces.

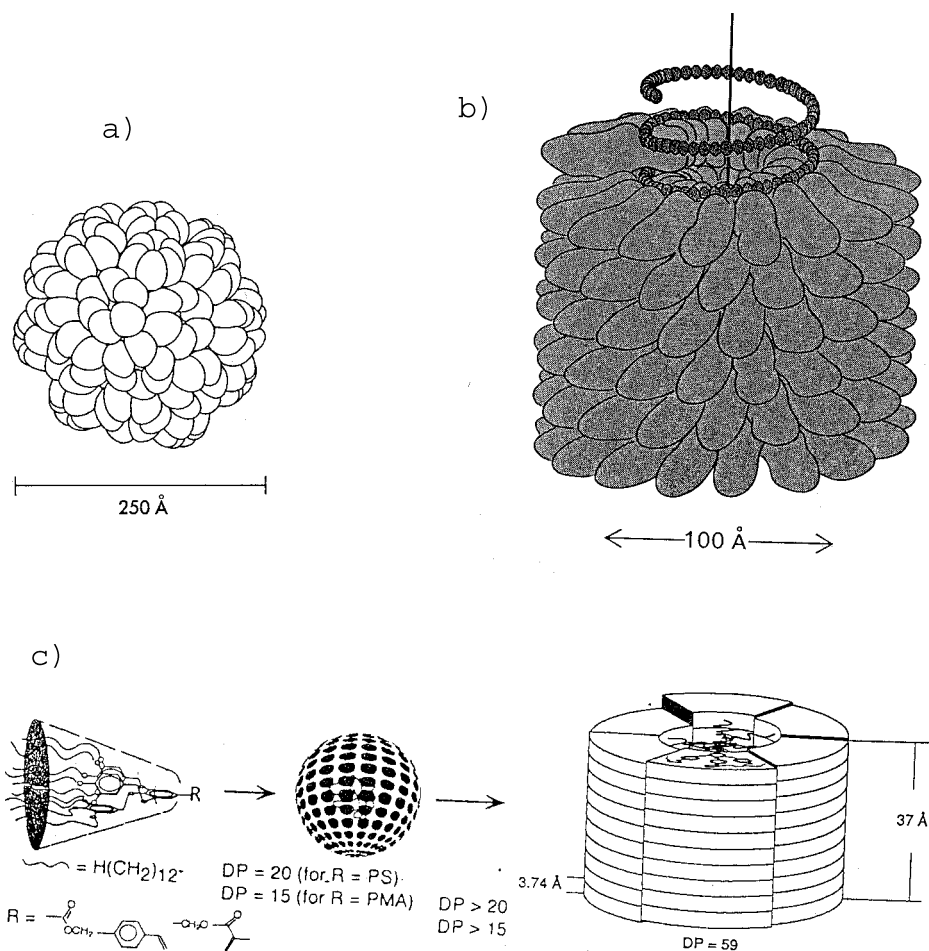


Fig. 1. Some natural and synthetic supramolecular systems: a) icosahedral virus, b) tobacco mosaic virus, c) self-organization of monodendrons jacketed polymers. (PS: Polystyrene; PMA: Polymethacrylate; DP: Degree of Polymerisation)

Figure 1 depicts some natural and synthetic supramolecular systems with cylindrical and spherical shapes.^[1-7] It shows the capsid structure of a small icosahedral virus that contains 180 identical proteins (MW about 14,000 daltons) cubically arranged about an inner RNA molecule with 3569 nucleotides (a) and the structure of tobacco mosaic virus, which has about 2150 identical protein molecules (MW about 17,000 daltons) helically arranged around a central RNA molecules containing approximately 6000 nucleotides (b). Stability of both structure in Figures 1a and 1b is achieved by forming a maximum number of bonds and by using the same kind of contacts again and again. Given these requirements, the resulting structure must be symmetric. In fact, all small viruses are either rods or spheres (or a combination on these shapes). Recently V. Percec and A. D. Schluter et al. independently proposed a strategy for the systematic design and synthesis of macromolecules by a covalent coating of conventional polymer backbones with dendritic side groups which self-assembly into spherical and cylindrical conformations (c), which were proved by x-ray analysis and SFM investigation. It became obvious that dendritic side groups are ideal candidates to control the conformation of synthetic polymers.

1.1. Principles of the synthesis of dendrimers and dendronized polymers

Dendrimers have received considerable attention as a new class of macromolecules.^[8-16] This interest is due to their highly and regularly branched structure, which may result in a variety of new and improved properties. Figure 2 presents the general structure of a dendrimer.

There are two fundamentally different approaches to synthesize these molecules. The first is the divergent growth method. It involves the initial reaction of an AB_x building block (B must be protected) with a polyfunctional core followed by activation of the peripheral functional groups B. Repetition of this two step process allows growth to proceed from the core outward with a rapid increase of the number of reactive groups at the periphery. Extensive reviews of this approach has appeared.^[17-18] A second route to dendritic macromolecules involves a convergent process^[19] in which growth begins at

what will become the periphery of the final macromolecule and proceeds inward, the final reaction being attachment of dendritic wedges (dendrons) to a polyfunctional core. The convergent growth approach offers a number of advantages over the divergent-growth one, such as involvement of a very limited number of reactive sites, ease of purification and characterisation. The limitation of the convergent growth approaches is that, as the sizes of the dendrons increase, the steric situation at the focal point becomes increasingly more congested. Large dendrons may simply wrap the functional group at this point and, thus, prevent further growth by attachment of another dendron. This limitation is not as significant with the divergent or starburst approach.

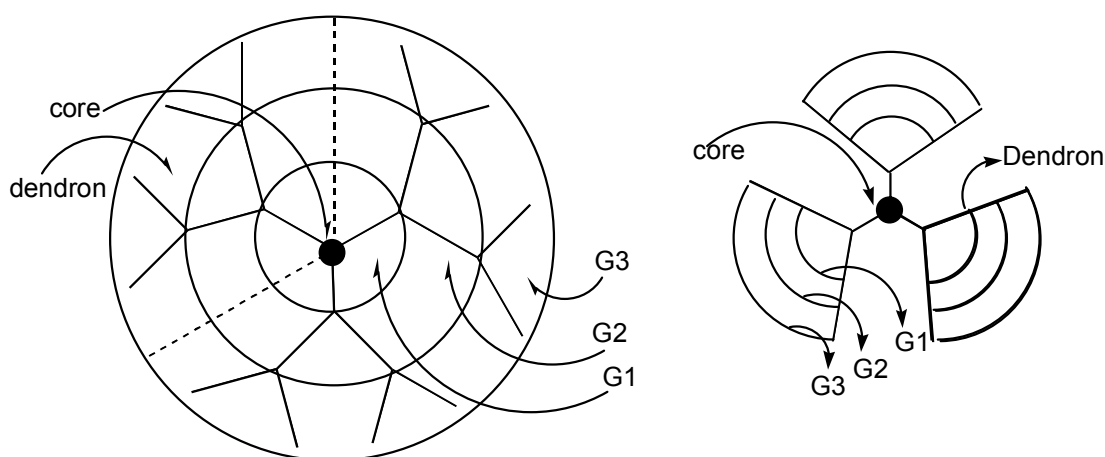


Fig. 2. Two different representation of the structure of a dendritic macromolecule(Dendrimer). Core: Oligo-functional centre part (1); Dendron: Branched wedges attached to core; Generation: Branching unite. G1: Generation 1; G2: Generation 2; G3: Generation 3.

Since their discovery some 20 years ago, dendritic macromolecules have stimulated an almost explosive research effort, and many related synthetic, analytical and application-related issues have been addressed.^[13] Even industrially applicable syntheses were developed.^[14]

Dendronized polymers are a new class of comb-like polymers with the comb's teeth being dendrons. Figure 3 displays a structure of this kind of polymer. Based on the

above discussion of the shape of dendrimers, one could expect that dendronized polymers under certain circumstances, attain cylindrical shapes as the cartoon (Figure 3) illustrated. The requirements for this would be: (a) a dense sequence of dendrons along the backbone and (b) maximum space demand of each dendron. As can be seen, the polymer backbone stretches out when the dendritic layer is so densely packed around the backbone. This results in a molecular cylinder to which a 'surface' can be assigned.

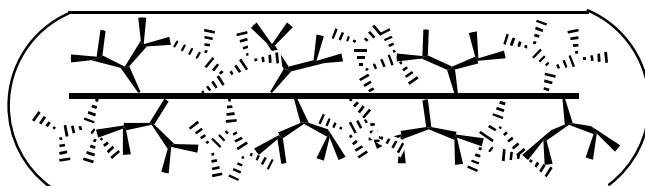
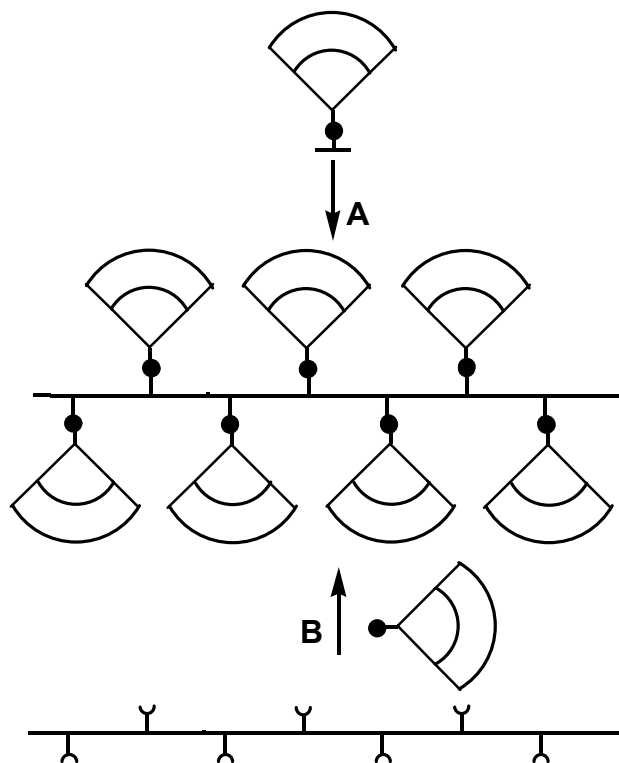


Fig. 3. Cartoon representation of a dendronized polymer with such a dense layer of dendrons around the backbone that the polymer's shape becomes cylindrical.

To clarify an often encountered misunderstanding, it is pointed out here that there is a distinct difference between a dendrimer and a dendronized polymer. Dendrimers are by definition (and if their structure is perfect) strictly monodisperse, whereas dendronized polymers are polydisperse. In this sense, this latter class of macromolecules do not represent dendrimer but rather polymers with unusual (dendritic) side chains.

Dendronized polymers first appeared in a US patent^[20] entitled 'Rod-like Dendrimer' filed by Tomalia and Kirchoff in 1987, and were proposed as being useful in the production of molecular composites and as crystallinity modifiers for polymeric materials. It is apparent that these compounds not only complement dendrimers with small cores under structural aspects, but as a consequence of the structural differences they should also have unique properties. Generally, two principally different synthetic routes can be used in the preparations of dendronized polymers (Scheme 1). In the first route (Route A), monomers already carrying dendrons are subjected to polymerisation or polycondensation. In the second route (Route B), the polymer which becomes the core in the final product serves as starting material. The anchor groups of this polymer are used to either divergently or convergently attach a dense sequence of dendrons

(attach-to route, Route B). The respective advantages and drawbacks for both routes will be discussed later (Chapter 5.1)



Scheme 1. Two routes to dendronized polymers: (A) the macromonomer and (B) the convergent routes.

1.2. Modification of dendronized polymers

Controlled surface modification of dendronized polymers (Fig. 4) is a challenging goal for both synthesis and many application-related issues. By surface modification, it is possible to tailor properties of the resulting polymer. For example, a dendritic cylinder soluble in organic solvents can be converted into a water soluble analogue by a simple synthetic step.

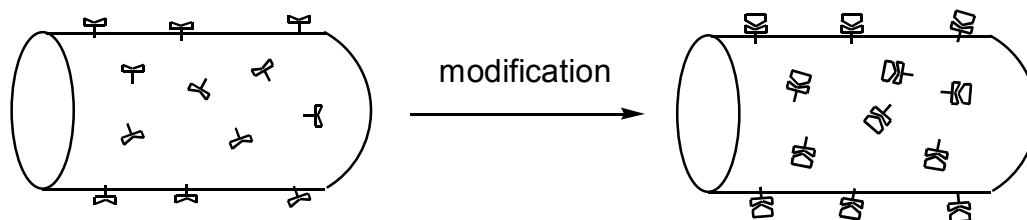


Fig. 4. Surface modifications of dendritic cylinder.

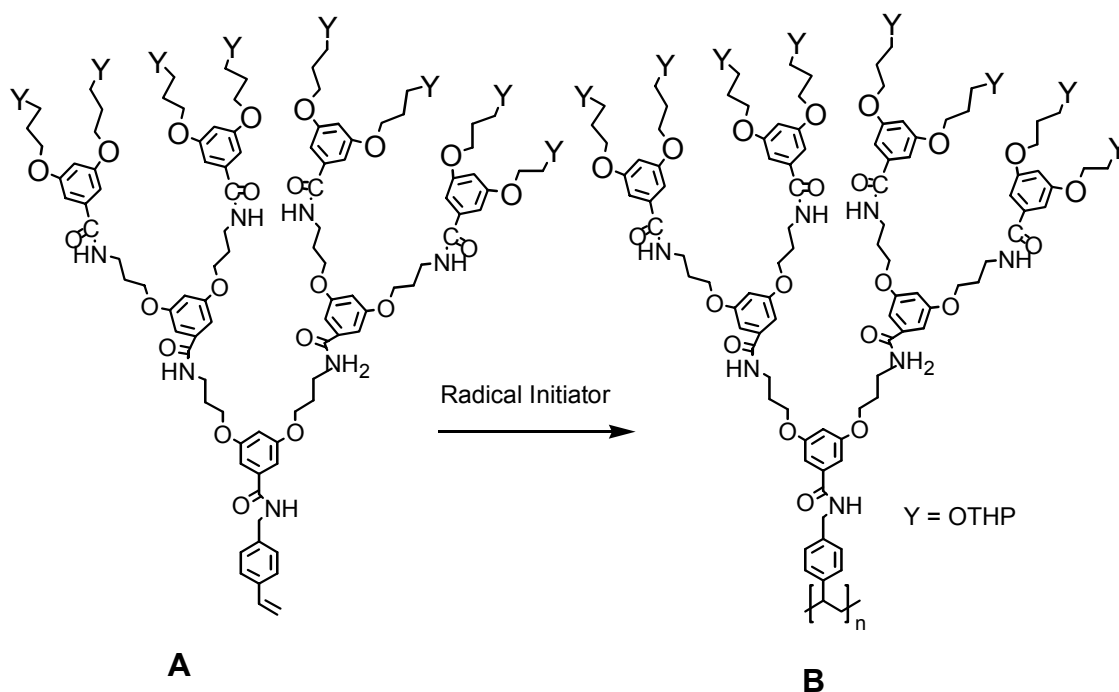
In the last few years, spherically shaped dendritic macromolecules with functional groups in the periphery were modified (or functionalized) with many specific reagents. This has led to a variety of dendrimers with identical skeleton but which exhibit a broad range of properties (glass transition temperature, adhesion, solubility etc.).

Some progress along these lines has also been achieved with dendronized polymers. For example, G1 and G2 dendronized polyacrylate bearing amino functional groups in the periphery were reacted successfully with activated amino acids. This should open an avenue for further modifications.

1.3. Goals of this thesis

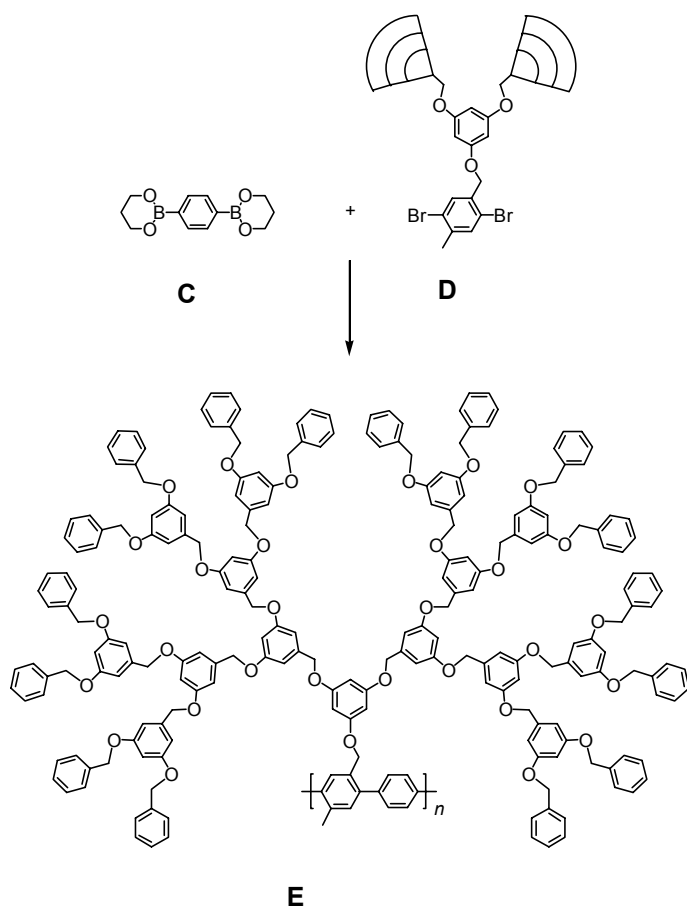
The synthesis and characterisation of dendronized polymers is one of the main projects in our group. Some initial results were achieved in this field. For instance, polystyrene bearing G1 and G2 dendrons with protected functional groups were prepared with reasonable molecular weights, and even a styrene monomer with G3 dendrons carrying protected hydroxyl groups could be polymerized to a low molar mass polymer ($P_n = 7$, $P_w = 20$) (Scheme 2). The resulting polymer was deprotected to yield the corresponding one with hydroxy groups at the periphery (the outer layer of the cylindrical polymer).

The other recent progress in this project was the successful synthesis of a G4 polymer by Suzuki polycondensation (SPC). The synthetic route is given in Scheme 3. Because the molecular weight difference between the two AA and BB monomers, it was difficult to meet in practice the 1:1 stoichiometry strictly required for polycondensations. For that purpose, G4 monomer **D** was prepared on the 20 g scale. This allows to do SPC on a



Scheme 2. Polymerisation of a G3 monomer with THP protecting groups. (THP = tetrahydropyran)

relatively large scale, thus ensuring sufficient stoichiometry control. In a series of experiments, optimal conditions were finally found which gave the corresponding polymer **E** with $P_n = 25$ and $P_w = 125$ [according to gel permeation chromatography (GPC)] on a gram scale. Presently, fractions of this material with $P_n = 10, 75, 150$ and 300 (GPC) are being investigated by small angle neutron scattering (SANS) in order to determine the true molar mass.^[21]



Scheme 3. Synthesis of a G4 polymer by SPC using the AA/BB approach.

Dendronized polymers can self-assemble on surfaces into highly ordered layers, which renders them into a material attractive for various applications. The assembly process can be investigated on the molecular scale using scanning force microscopy (SFM). Measurements of individual polymer chain are also in progress. In addition, the SFM

may be used to manipulate single macromolecules on solid substrates in order to generate assemblies, which would not form spontaneously.

Although some advance has been made, there were still urgent problems to be solved. As can be seen in the two examples above, for the first case, the molar mass is not high enough, especially for the visualisation of individual polymer chain by SFM. For the second example, because there are no functional (or potential functional) groups at the periphery of the polymer, it makes surface modifications impossible.

Considering these basic weakness, the goals of this thesis is clear. They are: a) to synthesize new dendritic macromomers in order to learn about general aspects of their polymerisation; b) to synthesise dendronized polymers with functionalities, higher generations and molar masses; c) to explore the feasibility of surface modification to furnish novel properties with these unusual polymers; d) to investigate the behaviour and properties of these dendronized polymers, especially to visualize the individual polymer chain by SFM and manipulate it on the surface by SFM tip.