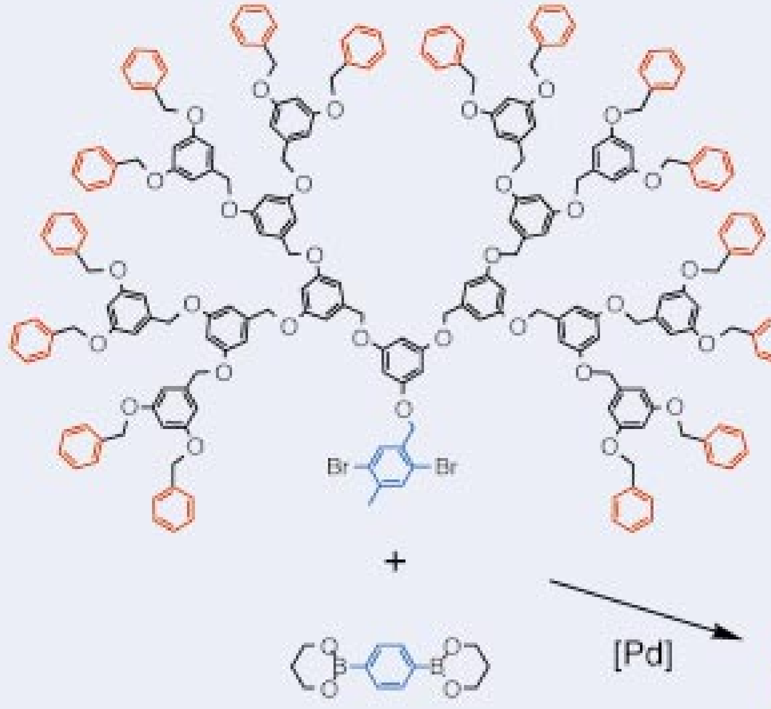
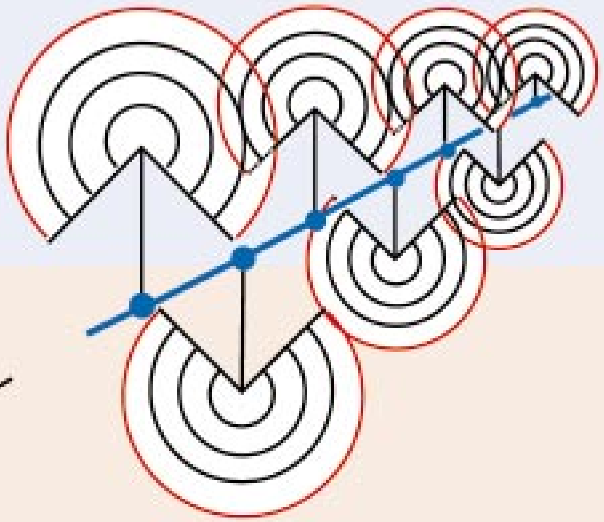
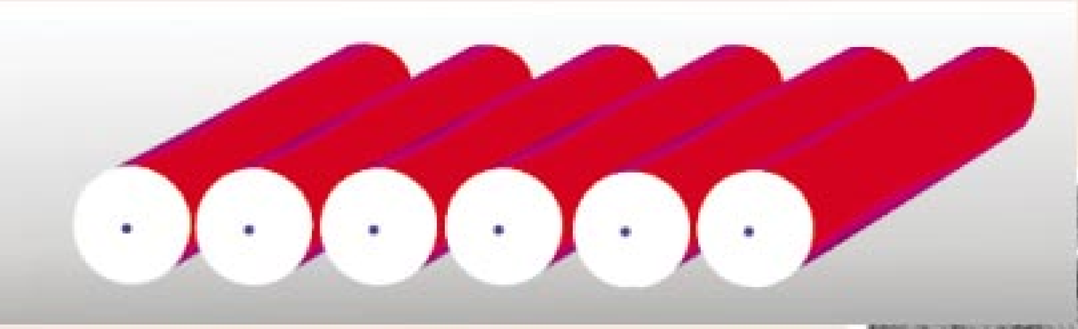
SPC

Suzuki Polycondensation



Nanoobjects





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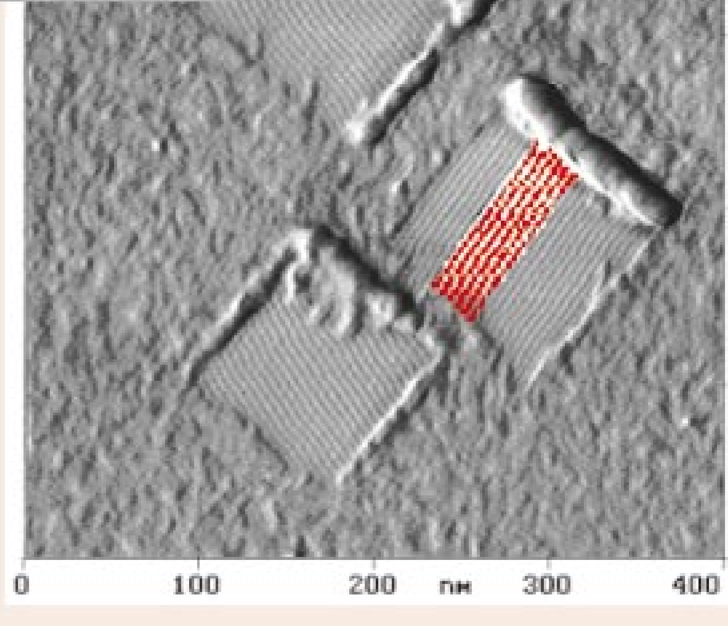
SFM

Scanning Force Microscopy



Dendronized Polymers: Synthesis, Characterization, Assembly at Interfaces, and Manipulation

A. Dieter Schlüter* and Jürgen P. Rabe*

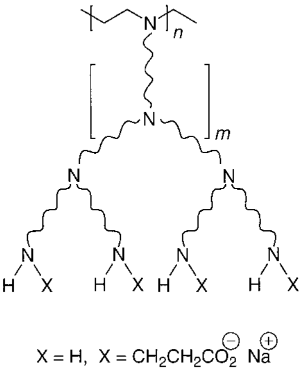
Dedicated to Gerhard Wegner on the occassion of his 60th birthday

Dendrimers are presently one of the most intensely studied classes of compounds because of their unusual structure. They can be described as a jungle of entangled branches traversed by winding trails which lead to sweet fruits and bright blossoms. On these trails one can reach the thicket's interior as well as find a way out. Expressed less lyrically, this thicket stands for regularly branched, densely packed structures, and the trails represent voids and channels not filled by bent back branches but by solvent. The fruit and blossoms are photochemically, electrochemically, or synthetically addressable units, catalytically active sites, etc., and the back and forth on the trails stands for transport processes. In a mathematical sense dendrimers are enveloped by an interface, which defines what is either in or out. This interface is shaped like a sphere if the trails are filled to bursting. Otherwise dendrimers are more flattened like amoeba, especially if in contact with a surface. The high density of the functional groups, the expansion of these compounds to a range of several nanometers, the existence of usable "surface" and transport possibilities in and with them have made dendrimers interesting candidates for many applications. This review describes how dendrimer construction and polymer synthesis were combined and used to move from fully or flattened spherical shapes to cylindrical ones. The shape-inducing influence of dendritic substituents can be driven to create nano-objects with a cylindrical shape, which not only considerably widens the range of applications for the dendrimer class but also opens up new perspectives for supramolecular and polymer chemistry. Because of the sheer size of the described objects and complexity of shape-related properties, research in this area must necessarily be interdisciplinary. This article tries to mirror this by giving special attention not only to synthesis but also the characterization and behavior of these compounds in bulk and at interfaces. Furthermore, potential application fields are described.

Keywords: dendrimers · interfaces · nanostructures · polycondensations · scanning force microscopy

1. Introduction

Practically all dendrimers[1] known today have cores with a few functional groups to which the corresponding number of dendrons (dendritic wedges) are attached. The fact that these dendrons are connected to one another by a small, almost dotlike molecule results in considerable steric congestion around the core. This congestion is a unique structural feature and has led to the viewing of dendrimers, specifically those of high generation, as molecular boxes or containers[2] and as entities that assume a spherical shape to which a "surface" can be assigned. The term surface may, of course, only be applied with care. Since their discovery some 20 years ago, dendritic macromolecules have stimulated an almost explosive research effort and many synthetic, analytical, and application-related issues have been addressed.[1] Even industrially applicable syntheses were developed.[3] During this stormy process research has almost exclusively been focused on dendrimers with small cores, in spite of a US patent entitled "Rod-like Dendrimer" filed by Tomalia and Kirchhoff in 1987.[4] There the dendrimers are like **1**, with polymeric



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cores, and were proposed as being useful in the production of molecular composites and as crystallinity modifiers for polymeric materials.[4] It took several more years before first (published) steps were undertaken to obtain these dendrimers.[5] It is immediately 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 (Sections 4 and 5). A simple reason for this slow development may be that in the beginning of dendrimer research spherical dendrimers were simply considered a more appropriate and perhaps more important target. Judging from the increasing number of publications, this view is presently undergoing some modification. Another reason may be seen in a reluctance to begin working on a seemingly more complex area than small-core dendrimers, where chemists are already being confronted with considerable synthetic and analytical difficulty.[6]

This article shows that the synthetic and analytical problems associated with dendronized polymers are not outrageously more complex than for small-core dendrimers, and that the difficulties can be overcome. It tries to draw a comprehensive picture of what has been done in the field of dendrimers with polymeric cores, putting emphasis on synthetic issues, on accurate molecular weight determination, and, finally, on the aggregation behavior of these intriguing macromolecules both in the bulk and at solid and fluid interfaces. The article starts with a short section summarizing some of the ideas why dendronized polymers make up a challenging project and where these unusual molecules are expected to have impact on the natural sciences.

The macromolecules treated here may be considered as either dendrimers with polymeric core or alternatively dendronized polymers (or polymers with appendent dendrons) depending on whether one sees them from the vantage point of an organic or macromolecular chemist (Figure 1). The first view is somewhat misunderstable, because dendrimers are normally considered monodispers (which they certainly are not[6]) whereas polymeric dendrimers are intrinsically polydispers. At best the polymeric core may have a narrow molecular weight distribution. Not considered here are polymers which do not carry dendrons at every repeat unit, but only at a few, for example at the two termini,[7] as well as work on surface coatings with dendrons or hyperbranched molecules.[8] The references to dendrimers with a dotlike core are kept at a minimum, and the reader is referred to pertinent reviews and monographs.[1, 9] A long[10] and a short review[11] on dendronized polymers are available. The present review covers also the many important developments in synthesis and characterization that have taken place in this rapidly moving area. Attempts to stiffen polymer chains by attaching flexible, straight oligomers to each repeat unit are not covered in this article due to space limitations.[12]

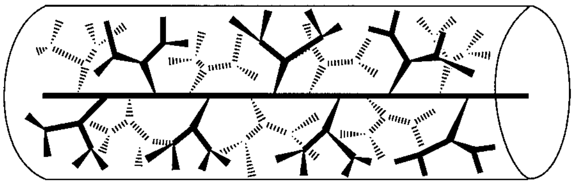

Figure 1. Cartoon representation of a dendronized polymer whose dendritic layer is so densely packed around the backbone that the backbone stretches out and a molecular cylinder with a "surface" is generated.

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Jürgen P. Rabe, born in 1955, studied physics and mathematics at the RWTH Aachen. After completing his diploma thesis with Prof. P. Grosse, he joind the biophysics group of Prof. E. Sackmann at the TU München, where he received his doctorate in 1984 for work on interface optics in lipid bilayers. He then joined the IBM Research Center in San Jose, CA, where he carried out STM experiments on ultrathin organic layers. In 1986 he joined the research group of Prof. G. Wegner at the Max Planck Institute for Polymer Research in Mainz. He finished his habilitation in physical chemistry in 1993 and became a Professor at the University of Mainz. In 1994 he accepted a chair in the physics department at the Humboldt University of Berlin, where he has remained since. His current research interests include the structures, dynamics, and properties of macromolecular nanostructures, spectroscopy of single molecules, molecular electronics, and scanning probe microscopies.

2. Dendronized Polymers—What Are They Like and What Are They Good For?

Dendronized polymers are formally comb polymers,[13] with the combs' teeth being dendrons. What makes them so unique that one does not normally refer to them as such? Mainly it is the complex interplay of dendron size, distance between dendrons, and backbone flexibility or rigidity together with several interactions (e.g. dendron/dendron, dendron/backbone, solvent/dendron). All these factors sum up to a slower decrease in density on going from the interior to the exterior than in common comb polymers where the teeth are linear chains.[14] This unusual density profile leads to new and rather fascinating properties of otherwise conventional polymers. The first issue to mention here is the shape of the polymer and its dependence on the substitution with dendrons. Depending on the dendrons' structure, size, and attachment density along the backbone, conventional polymer backbones such as polyacrylate or polystyrene can attain conformations all the way from random-coil to fully stretched linear: A flexible, (cooked!) spaghettilike polymer can be converted into a rigid (i.e., with a high bending modulus) rod just by proper substitution with large dendrons. This stiffening of the backbone is caused by steric repulsion between the pendant dendrons. For that reason the whole matter is referred to as shape control by implementation of steric strain. In this sense steric strain may be compared to hydrogen bonding and π,π stacking as the corresponding shape-determining factors in proteins or DNA. In the extreme case, which will be described in Section 5, the dendritic layer around the polymer backbone is so dense that a macromolecule can turn into a molecular cylinder with defined dimensions: Its length is determined by the degree of polymerization and its diameter is roughly two times the dendron extension. In this case the dendrons spread away from each other to keep steric repulsion between them at a minimum.

Dendronized polymers can, however, also be designed so that there is an attractive interaction between dendrons that leads to shape control. This requires two features: a) dendrons with mesogenic properties and b) their loose attachment to the backbone, which leaves the dendrons sufficient freedom to find the optimum packing. This kind of shape control driven by the mesogenic properties of the dendrons can lead to highly ordered materials in the solid state, as will be described in Section 4.

Let us come back to rigid polymers with a tightly packed dendritic layer around the backbone. What is the importance of such cylindrical objects? Two issues which immediately come to mind here are rigidity and surface. In contrast to conventional polymers their diameter is on the order of a few nanometers rather than a few angstroms. As a consequence the rigidity is so high that the persistence length of an individual chain is not on the order of 10 nm, but may instead exceed 50 nm. Thus, exceptionally high bending moduli can be expected, despite the fact that the polymers are still single-stranded. Dendritic rods could therefore potentially be used for constructions on the nanometer scale, very much like an architect builds frames for houses or bridges from plywood. The first steps in this direction would be to isolate individual rods, to determine their dimensions, and to move them about. Developments in this direction will be described in Section 5. So far individual molecules have been adsorbed to atomically flat surfaces. The high modulus results in a very strong tendency of these rods to form large, ordered, two-dimensional arrays in which the individual rods are packed parallel to each other like tree trunks of a raft, the only difference being that the dendritic "trunks" have a length distribution. Such large, parallel-ordered, nanometer-scale objects on surfaces are interesting for a number of applications, for example as polarizers, polarized emitters, or orienting surfaces in liquid crystal displays.

Apropos tree trunks and cylindrical surface: This may be also a starting point to think about dendritic rods as supports with defined curvatures to which catalytically active components could be attached. In a way cylinders of the size discussed here bridge the gap between homogeneous and heterogenous catalysis. They may combine the advantages of both. Attachment of catalytically active groups to the surface at more or less constant distances may well provide candidates, for example, for applications in flow reactors. Spherically shaped dendrimers equipped with transition metal complexes have already been successfully employed for such purposes.[15]

At a first glance, the fact that the tobacco mosaic virus also has a cylindrical shape[16] is a somewhat artificial link to the biosciences, but this striking similarity may nevertheless help initiate thought about the potential biological importance of dendritic rods and derivatives thereof.

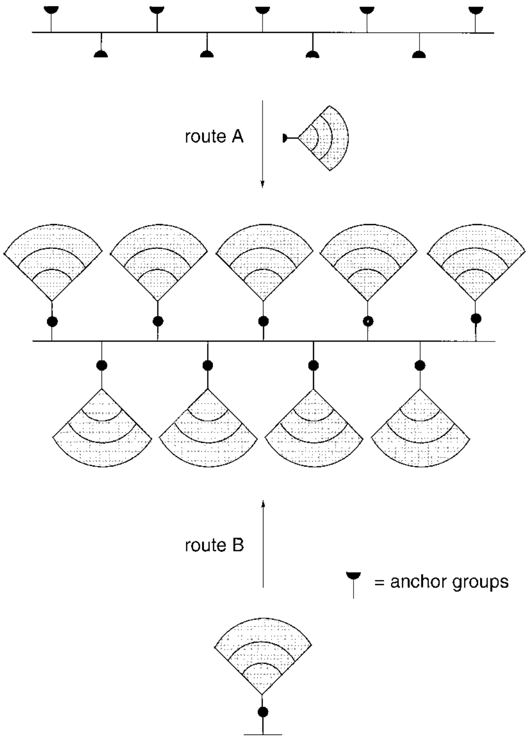
In Section 5.2 we describe first steps towards another important application of dendritic cylinders. Common amphiphiles such as dodecylsulfonate can form micelles, bilayers, and other interesting and sometimes even commercially relevant supramolecular aggregates.[17] These amphiphiles normally are a few nanometers long and have diameters of a few angstroms. If it were possible to decorate the surface of a dendronized polymer with one hydrophilic and one hydrophobic block that is segregated perpendicularly to the backbone, giant amphiphiles would result, which may lead to a big jump in the size of the corresponding aggregates. Alternatively, if it were possible to decorate the cylinders not cross- but lengthwise, the resulting amphiphiles would have the unique polarity distribution of some ion channel membrane proteins, and could be used as coatings to reverse surface polarities or for various applications as colloids.

Last but not least, the issues of synthesis and structural analysis ought to be mentioned. Before chemistrs can enter into all the exciting options mentioned above, dendronized polymers need to be synthesized and sufficiently characterized on both the organic chemistry and polymer level. Without going into details the main synthetic problems include a) steric repulsion and thus incomplete reactions; b) autocatalytic decomposition of sensitive dendrons because of their exceptionally high functional group density; c) high molar mass and sometimes large differences in the molar mass of reactants, which makes it difficult to meet correct stoichiometry; and d) purification of high molar mass reactants. These factors may appear almost trivial, but can brew together to a seething mixture which renders a controlled synthesis quite an endeavour and challenge. Additionally, the size of the molecules involved makes the tools of organic chemistry absolutely insufficient. Additional methods like small-angle neutron scattering (SANS), scanning force microscopy (SFM), X-ray diffraction, and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry need to be employed to really prove what one proposes to have.

3. Synthesis

3.1. General Considerations

There are two principally different synthetic routes to dendronized polymers (Scheme 1). In the first route, 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 A). In the second route, monomers already carrying dendrons are subjected to polymerization or polycondensation (macromonomer route, route B). The intrinsic problems of both routes become more serious and limiting, the more sterically demanding the dendrons are. An obviously critical issue associated with route A is achieving complete coverage of the backbone anchor groups with dendrons. Even if a very efficient coupling chemistry is available, a large excess of dendron may be required to drive the reaction to completion. This excess may, in turn, make it difficult to purify the product. If large dendrons are to be attached, steric hindrance also comes into play for two reasons: a) the shielding of unchanged anchor groups on the backbone by dendrons already attached in close proximity and b) the conformation of the dendron, which may lead to a self-shielding of the functional group at the focal point through which the attachment ought to take place. Both factors lead to a decrease in the rate of attachment, if they do not suppress the process entirely. This decrease of rate can favor side reactions which may not just involve themselves or the solvent but also the already attached dendrons.



Scheme 1. The two routes (A and B) to dendronized polymers. The dendrons shown are of generation three (G3).

The problems associated with route B also have something to do with steric hindrance. Here the critical point is the steric demand of both monomer and chain end. Incoming monomer will only be connected to the chain end if the steric hindrance is not too high. Otherwise this process will be slowed or even rendered impossible. Depending on the kind of polyreaction applied, this may lead to termination of the reactive chain end and/or to side reactions of the monomer, such as loss of coupling functionality, as in some polycondensations, or auto-initiation, specifically in radical polymerizations. From this discussion it can be extracted that the basic problems for both routes are: incomplete coverage (route A) and low molecular weight dendronized polymer (route B).

Besides hurdles to synthesis there are also hurdles to analysis. Dendronized polymers tend to have repeat units (RU) of considerable molecular weight. Repeat units with 1, 2, or even 3 kDa are no exception. Such high molecular weights sometimes render structural characterization difficult, because the proportion of backbone to dendron atoms becomes so unfavorable that NMR spectroscopy reaches its limits. For example, sometimes the degree of attachment (coverage) simply cannot be determined with sufficient accuracy, because the signal intensity of the unchanged anchor groups is too weak for comparison with reference signals in the spectrum. NMR characterization may occasionally be further complicated by large differences in the relaxation times of backbone and dendron nuclei. Thus, integrals of NMR signals are rendered unreliable if a sufficient pulse delay time is not applied.

Another problem with dendronized polymers is their molecular weight determination (Section 3.3). Gel permeation chromatography (GPC) is a quick and easy method to roughly estimate the molar mass of a polymer.[18] This estimation can only be reasonably used as long as the hydrodynamic volumina of the polymer under consideration and the polymer used for calibration purposes, typically polystyrene (PS), are in the same range. The hydrodynamic volume of dendronized polymers strongly deviates, however, from polystyrene, and GPC results should be treated with care. Additionally, facile aggregation of these dendrimers is sometimes encountered, which leads to further complications. Other methods of molecular weight determination such as light scattering have to be used and measures taken to avoid aggregation.

Looking back over what has happened regarding synthesis of dendronized polymers since 1992, when one of the authors (A.D.S.)[5a] and Percec et al.[5b] independently started working in this field, one has to arrive at the conclusion that the attach-to route (route A) is inferior to the alternative macromonomer approach (route B). There is no reported case of route A in which complete coverage of a polymeric core with dendrons of higher generation than G2 was achieved. Additionally the polymeric cores used (mostly of the poly(*para*-phenylene) (PPP) type) did not have very high molecular weights. For route B, however, many cases of high molecular weight G2 compounds and one case of a G3 compound are known. Furthermore, the case of a high molecular weight G4 compound was reported very recently. It is for that reason that this article concentrates on the latter case. For a recent treatment of representatives of route A, the reader is referred to another review.[10]

3.2. Overview of the Macromonomer Approach

The synthesis of dendronized polymers from macromonomers (route B) has been developed broadly in recent years. A reason for this is the advantage that polymers, if they can be obtained at all by this method, necessarily carry the predetermined number of dendrons at the backbone. The above questions of dendron perfection and degree of coverage in divergent and convergent syntheses do not play a role. This only holds true, of course, if the dendrons are compatible with the polymerization conditions, a prerequisite which is fulfilled in many of the cases reported. The polymerization procedures used can be divided into a) radically initiated and transition metal catalyzed chain growth and (b) step-growth polymerizations (polycondensations). Figure 2 gives an overview of the macromonomer structures reported to date and groups them into the subclasses a and b depending on the respective type of polyreaction. Fréchet-type dendrons[19] are drawn in an abbreviated form, which is explained in Figure 3. The monomers are polymerized by radical polymerization (**2**,[5b, 20] **3**,[21] **4**,[22] **5**,[23] **6**,[24] **7**,[25, 26] **8**,[27] **9**,[28] **10**,[24] **11**,[29] and **12**,[30]), insertion polymerization (**13**[31]), ring-opening metathesis polymerization (ROMP)[32] (**14**[33, 34]), Suzuki polycondensation (SPC)[35] with **17** (**15**[36] and **16**[37]) and **23** (**20**,[38] **21**,[39] and **22**[39]), polyaddition with **19** under polyurethane formation (**18**[40]), and Heck coupling of **24** with **25**.[41] Dendronized oligomers with enediine RUs were also prepared.[42]

Some features of the dendronized polymers obtained from the macromonomers of Figure 2 will become important later in this article and are therefore emphasized in the following: a) Most of the macromonomers carry G1 or G2 dendrons. The only exceptions are **12**(G3), **16**(G3), and **18**(G3, G4) (see also Section 3.4). b) Many dendrons are of the benzyl ether type whose terminal phenyl rings are either unsubstituted or have between one and three long alkoxy or fluoroalkoxy chains. The corresponding polymers are important for a variety of reasons, but are unreasonable candidates, of course, whenever chemical modification becomes an issue. c) This is where dendrons **7**, **8**, **10**, **11**, and **13**, which carry protected functional groups (hydroxy, amino, trimethylsilyl (TMS)[43]) in the periphery, come into play. The corresponding polymers are the starting point for the important aspect of surface modification (Section 6). d) Finally, dendron **8**(G2) has one unpolar and two polar branching units, and dendron **11**(G2) is completely unpolar except for its terminal, protected amine groups. These structural features are viewed in the context of synthesizing dendronized polymers with specific polarity patterns, which will become an important matter in the future but will not be discussed in this review.

In contrast to common organic reactions, the concentration of the reaction medium plays an absolutely important role in the polymerization of macromonomers. This may go so far that below a certain concentration polymerization is not only slowed down but rather rendered impossible. This question will therefore be addressed in the following in some detail using monomer **8**(G2) as a representative example.[27] For this monomer the dependence of molar mass on concentration was investigated systematically for $c_m = 34-64\,\%$, where c_m is the concentration of monomer in weight percent. As can be seen from Figure 4 (p. 872), there is only a narrow concentration window in which polymerization proceeds satisfactorily. Below $c_m = 45\,\%$ the monomer practically does not polymerize at all; molar masses are in the oligomer regime and yields are poor. Molar masses and yields increase sharply between $c_m = 45$ and $53\,\%$, whereby the masses pass through a maximum. For concentrations higher than $c_m = 53\,\%$ yields remain more or less constant; molar masses, however, decrease quickly until a plateau is reached. Similar results were observed by Tsukahara et al. for macromonomers with oligostyrene side chains.[44] Additionally they observed threshold molarities [M], at which the steep increase occurs rapidly, and shifts to higher values as the molecular weight of the macromonomer decreases. For monomers with roughly 12500 and 4.500 $\mathrm{g\,mol^{-1}}$ they observed threshold molarities of [M] = 0.04 and 0.1, respectively. Unfortunately the molarity of the solutions of monomer **8**(G2) could not be determined with sufficient accuracy for concentrations higher than 59 wt%, rendering a sound comparison of the above experiments with those reported by Tsukahara et al. impossible. Qualitatively, however, monomer **8**(G2) lies in the trend.

A possible explanation for the observed maximum may be that after a few growth steps the oligomer adopts a spherical shape with the radical chain end somewhere in its interior. At low molarity, this results in a sharp concentration gradient from the interior of the sphere to the surrounding solution, against which the monomer has to diffuse to achieve growth; in other words, the concentration gradient protects the radical chain end. As the monomer concentrations in solution and in the spheres (here: monomer = pendant dendron) become similar, a gradient no longer exists and further growth can take place. At even higher concentrations the viscosity of the medium increases, which limits the mobility of large monomers and thus favors termination.[45] For a kinetic analysis of the polymerization of G1 macromonomers, which led the authors to assume that their monomers self-assemble into molecular "reactors" prior to polymerization, see the work by Percec et al.[46] A recent review on poly(macromonomer)s is also available.[47]

This example makes impressingly clear how important it is to use unusually high concentrations and to carefully investigate the optimum concentration range. One simply does not get any polymeric material otherwise. This may be falsely attributed to detrimental steric congestion as the monomer approaches the reactive chain end and lead to the wrong impression that polymerization of a certain monomer is intrinsically impossible.

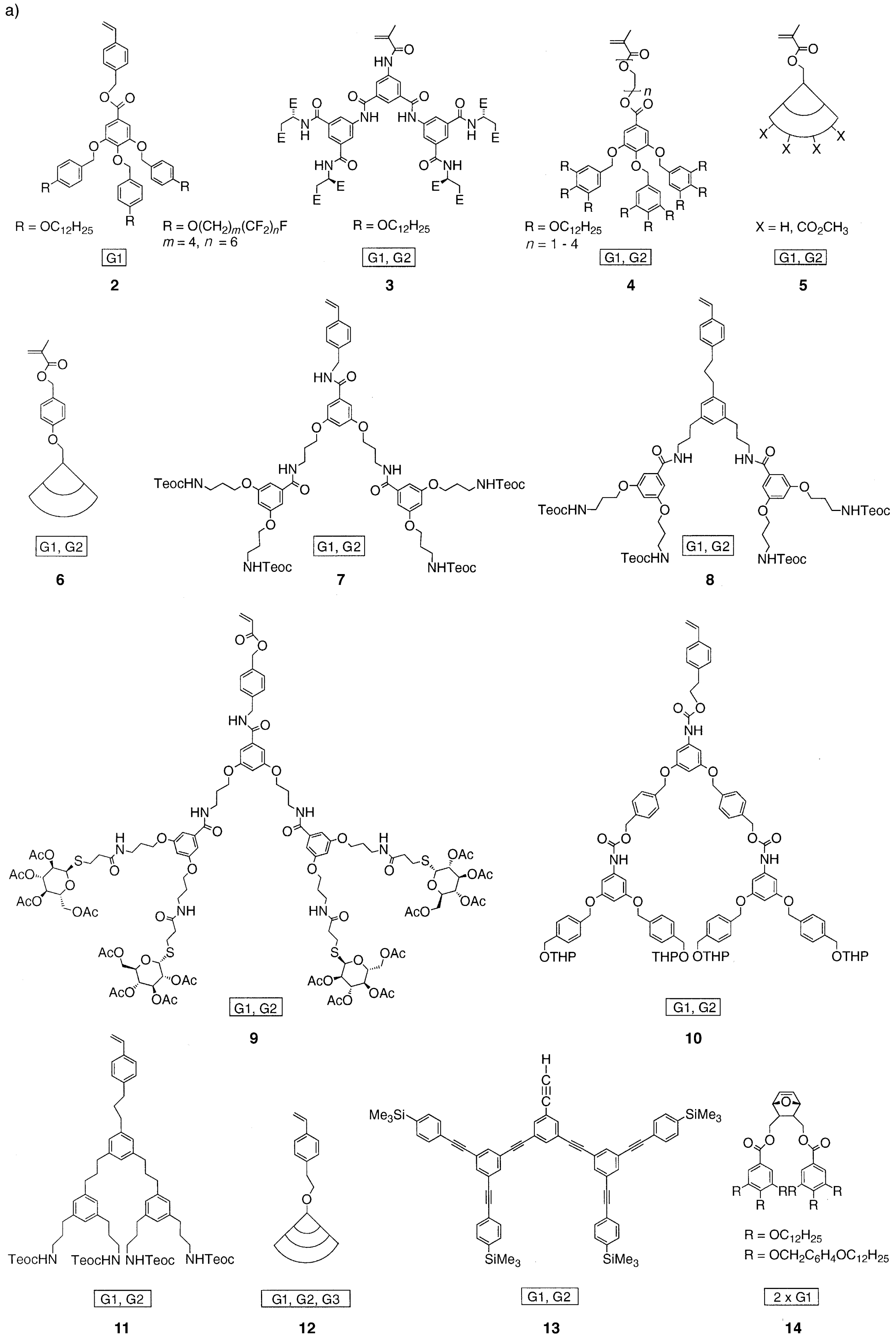


Figure 2. Structures of macromonomers used to obtain dendronized polymers by chain-growth (a) and step-growth procedures (b). THP = tetrahydropyranyl.

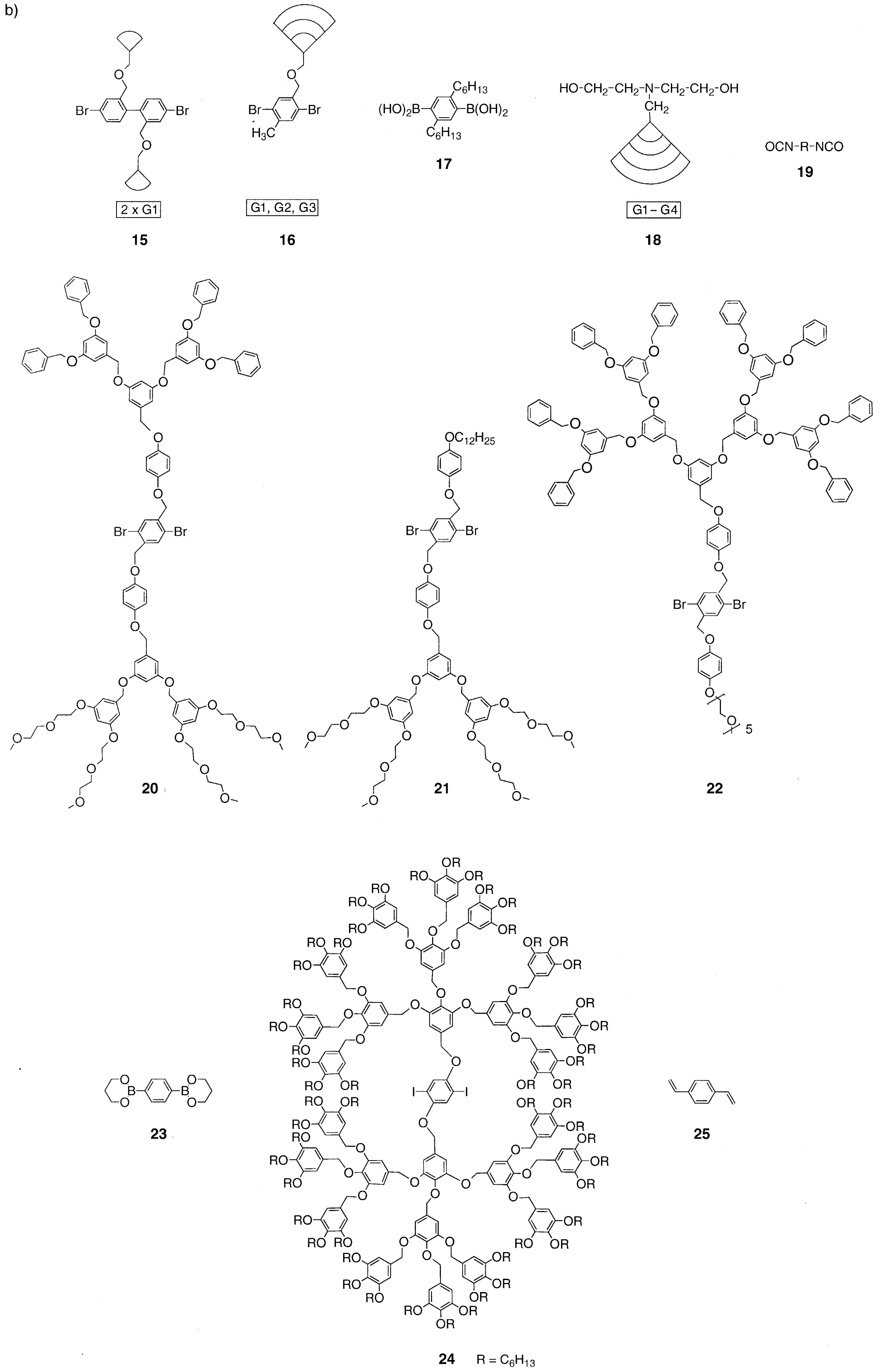


Figure 2. (Continued)

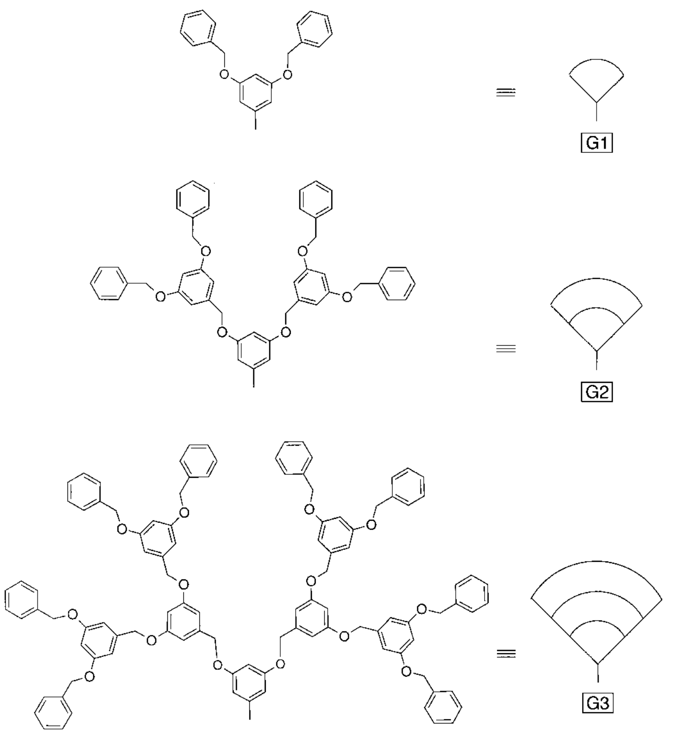


Figure 3. Fréchet-type dendrons (G1–G3).

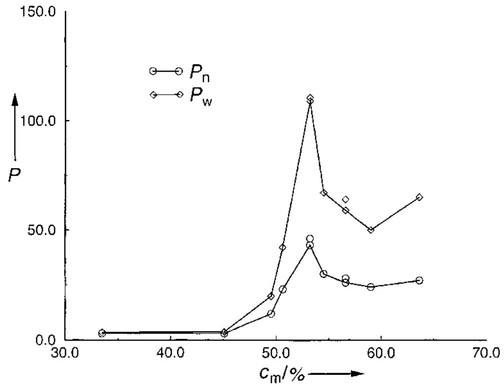


Figure 4. Dependence of the degree of polymerization (P_n, P_w) on the monomer concentration (c_m in weight %) for the polymerization of monomer **8**(G2).

3.3. Molar Mass Determination

Table 1 contains the molar masses of most of the prepared polymers. In practically all cases these values were obtained from GPC versus a polystyrene (PS) standard. As pointed out in Section 3.1 this is not an appropriate method for determining the molar mass of dendronized polymers. The values given

Table 1. Dendronized monomers, polymerization conditions, and molecular weights (determined by GPC) of the polymers obtained. The molecular weights are not comparable (see text).

Monomer	Conditions	$M_n \times 10^{-3}$	M_w/M_n	P_n	Yield [%]
2 ($R = OC_{12}H_{25}$)	AIBN, 60 °C, benzene	25–69[a]	1.7–2.5	23–58	44–72
2 [$R = O(CH_2)_m(CF_2)_nF$]	AIBN, 60 °C, benzene	23	1.2	12	65
3(G1)	AIBN, 60 °C, DMF	23	3.9	43	90
3(G2)	AIBN, 60 °C, DMF	–	–	≤6[b]	53
4[c]	AIBN, 60 °C	187	2.4	84	–
5(G1)	AIBN, 60 °C	9	2.6	24	70–80
5(G2)	AIBN, 60 °C	6	2.3	7	60
6(G1)	AIBN, 40 °C	270	2.2	544	75
6(G2)	DBPO, 60 °C	83	2.2	90	90
7(G1)	AIBN, 50 °C	110	2.9	166	97
7(G2)	DBPO, 60 °C	48	2.2	40	79
8(G2)	*t*BPB, 90 °C, toluene	65	2.4	46	93
9(G1)	AIBN, 55 °C, benzene	71	2.2	55	92
9(G2)	*t*BPB, 90 °C, toluene	12	1.03	5	46
10(G2)	*t*BPB[d], 90 °C	85	3.3	51	90
11(G1)	AIBN, 55 °C, toluene	38	2.0	60	85
11(G2)	*t*BPB, 90 °C, toluene	50	1.9	39	86
12(G1)	DBPO, 60 °C, toluene	25	1.9	56	60
12(G2)	DBPO, 70 °C, toluene	33	3.9	38	93
12(G3)	*t*BPB[d], 90 °C	62	6.7	36	70
13(G2)	$[\{Rh(C_7H_8)Cl\}_2]$, NEt_3	960	1.4	975	36
14 ($R = OCH_2C_6H_4OC_{12}H_{25}$)	$[RuCl_2(CHPh)](PCy_3)_2$, 22 °C, CH_2Cl_2	87	1.3	120	84
15 + **17**	$[Pd(PPh_3)_4]$, 2 N NaOH, toluene	18	3.8	18	80–85
16(G1) + **17**	$[Pd(PPh_3)_4]$, 2 N NaOH, toluene	19	3.6	29	90
16(G2) + **17**	$[Pd(PPh_3)_4]$, 2 N NaOH, toluene	21	2.8	19	89
16(G3) + **17**	$[Pd(PPh_3)_4]$, 2 N NaOH, toluene	52	5.3	27	96
18(G2) + **19**[e]	–[d]	17	3.0	17	98
18(G3) + **19**[e]	–[d]	21	4.2	12	97
18(G4) + **19**[e]	–[d]	24	3.0	7	92
20 + **23**	$[Pd\{P(p\text{-tolyl})_3\}_3]$, 2 N $NaHCO_3$, THF	38	2.3	20	98
21 + **23**	$[Pd\{P(p\text{-tolyl})_3\}_3]$, 2 N $NaHCO_3$, THF	28	2.0	20	96
22 + **23**	$[Pd\{P(p\text{-tolyl})_3\}_3]$, 2 N $NaHCO_3$, THF	21	1.9	10	94
24 + **25**	$[Pd\{P(p\text{-tolyl})_3\}_3]$, 2 N $NaHCO_3$, THF	35	1.6	12	–

[a] Dependant on the length of the ethylene oxide spacer, [b] Determined by MALDI-TOF mass spectrometry. [c] A related monomer based on acrylate gives higher molecular weights. [d] Without solvent. [e] $R = (CH_2)_6$. AIBN = azobisisobutyronitrile, DBPO = dibenzoyl peroxide, *t*BPB = *tert*-butyl perbenzoate.

should therefore be treated at best as rough guesses (see below in this Section), and a direct comparison of different polymers is impossible. This also holds true for polymers with the same backbone but dendrons from different generations. Nevertheless, some general conclusions can be drawn:

a) Monomers with more complex structures, like **3**, or those in which the dendron is bound too tightly to the polymerizable group, like **5**, do not give high molecular weight materials.[46]
b) Rh-catalyzed acetylene polymerization of **13** and Ru-catalyzed ROMP of **14** give the best results, along with a few of the radical polymerizations (**6**(G1), **4**).
c) There is a trend to decreasing molecular weights with increasing size (generation) of dendron.
d) The yields are not always high, which means that the corresponding polymerizations do not proceed well or that oligomeric products are formed, which are removed during workup. The latter point relativates some of the molecular weight values given.

Despite the importance of an accurate molar mass determination of dendronized polymers, a systematic study on this matter is not yet available. The most extensive investigation is one where GPC molar mass of five polymers obtained from monomers **7**(G1), **7**(G2), **12**(G1), **12**(G2), and **12**(G3) are compared with those obtained from small-angle neutron scattering (SANS).[48] Both fractions and representative samples of these polymers were employed. Table 2 summarizes the results. In all cases the SANS values are higher than those from GPC, and the factor by which GPC underestimates the real molar masses varies between 1.6 and 3.9. A qualitative explanantion for this finding is to be seen in the much larger mass per unit length of dendronized polymers than the calibration standard polystyrene. The true molar mass should therefore be higher than the GPC molar mass. There is, however, an opposing effect which has to do with the stiffening of the polymer chain imposed by the spatially demanding substituents. This leads to an increased hydrodynamic volume, causing the GPC molar mass to become larger than the actual molar mass. For the cases shown in Table 2 the latter effect obviously does not overcompensate the former. Whether this will still be the case for polymers with G4 substituents awaits to be seen. The SANS measurements also revealed that polymer **12**(G3) is a rigid rod whose persistence length is on the order of the contour length.

Table 2. Molar masses of dendronized polymers determined by GPC and SANS.

Polymer	$M_w \times 10^{-3}$		M_w(SANS)/	Length
	(GPC)[a]	(SANS)	M_w(GPC)	[nm]
P7(G1)	277	437[b]	1.6	3.8
P7(G2)	84	275[b]	3.3	5.0
P12(G1)	178	276[c]	1.6	3.1
P12(G3)	710	2530[c]	3.6	4.6
P12(G3)	59	233[c]	3.9	5.1

[a] In THF. [b] In CD_3OD. [c] In C_6D_6.

The degree of polymerization (P_n) of polymer **P16/17**(G3), a representative of a step-growth polymer (Figure 2b) obtained from monomers **16**(G3) and **17**, was also investigated carefully in order to learn about the effectiveness of step-growth procedures (here SPC[35]) in the case of sterically demanding monomers. Its P_n could not be directly determined because of unsurmountable problems with aggregation. Through some chemical modification, however, an average $P_n = 110$ was finally obtained. According to Carother's equation,[49] this P_n results when each coupling step proceeds with a conversion of 99.1%. From a synthetic point of view this finding is truly remarkable. It shows the enormous potential of SPC, even for cases where steric congestion is considerable, and has initiated further developments, which are described in the following Section.

3.4. Some Aspects of the Molecular Structure and Recent Progress in Suzuki Polycondensation (SPC)

As discussed in Section 2, one objective for research of dendronized polymers was to use the decoration with dendrons as a means to stiffen the backbone to the point that it is fully stretched. This goal should be reached when the individual dendrons are evenly distributed around the backbone and tightly packed at the van der Waals distance. Of course, the fully stretched conformation will also be reached with somewhat less tight packing, provided solvent molecules are diffused into the dendritic layer through osmotic effects. Both cases lead to a rigid rod with a cylindrical envelope; however, only in the first case would this shape be practically independent from the surrounding medium. In the second the dendritic layer would collapse under conditions where the solvent diffuses out (e.g. under vacuum). The question of tightness of packing is essential for synthesis. Generally speaking, the synthesis becomes more difficult, the less spatial mobility the reaction partners have to attain the mechanistically required relative conformation in the transition state of the reaction (here: growth step). To evaluate the feasibility of a certain polymerization on grounds of steric interactions, it would be ideal to have a detailed picture of the spatial changes around the reaction center on going along the reaction coordinate. Since it is practically impossible to obtain this with a reasonable amount of computational effort, only some molecular dynamics (MD) calculations of final products were performed. Additionally some polymers were visualized by computer-generated three-dimensional images in order to help the synthetic chemist to assess whether or not a macromonomer undergoes polymerization.

The MD simulations were performed in vacuo with polymers **P12**(G3)[50] and **P16/17**(G3),[51] which carry the same G3 dendrons but differ by the average distance between the dendrons' anchor groups (**P12**(G3): 2.50 Å, **P16/17**(G3): 8.25 Å) and the flexibility of the backbone (Figure 5). Unfortunately solvent molecules could not considered due to the enormous number of atoms already present in the polymers. Figure 6 shows the minimum conformations obtained. Whereas the dendritic layer of **P12**(G3) is quite compact, that of **P16/17**(G3) is much more open and loose. The diameters of **P12**(G3) and **P16/17**(G3) are on average approximately 4.4 nm and 2–4 nm, respectively. This difference in compactness is certainly to a large extent due to the

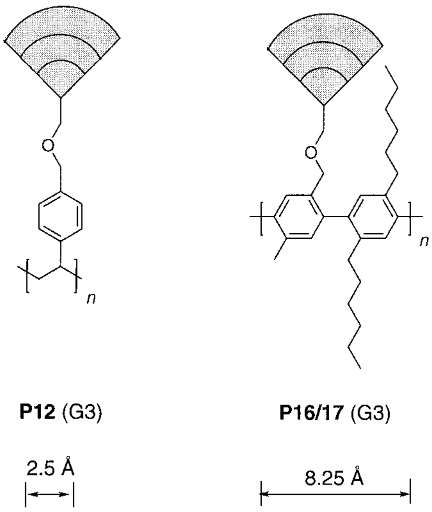


Figure 5. Polymers **P12**(G3) and **P16/17**(G3) along with the lengths of their repeat units (2.5 and 8.25 Å, respectively), which is required to qualitatively assess the average distance between attached dendrons.

different average distance of the dendrons' anchor groups at the backbones, but the different stiffnesses of the backbones also play a role here. Whereas the contour length of **P16/17**(G3) of the starting conformation upon equilibration remains practically constant, that of **P12**(G3) is reduced by some 30% when the minimum conformation is reached. This shows that the dense packing of the latter polymer can be partially attributed to some backbone coiling. It is reasonable to assume that it is exactly this small, still available space which rendered the polymerizations feasible. Considerations regarding preaggregation of polymerizable dendrons into ordered cylindrical arrays prior to polymerization through the aggregate[46] do not seem to be applicable here.

Figure 7 shows computer-generated structures of **P16/17**(G1) through **P16/17**(G4). Though these structures are not fully energy minimized, it is quite obvious that there is space between consecutive dendrons even for the G4 case. This space together with the surprisingly successful polymerization of monomer **16**(G3) supported the idea to also try SPC with monomer **16**(G4).

The attempt to subject a G4 monomer to SPC met with trivial but nonetheless serious synthetic difficulty, and it was not clear for a long time whether or not such a polycondensation could be brought about. Scheme 2 shows the finally

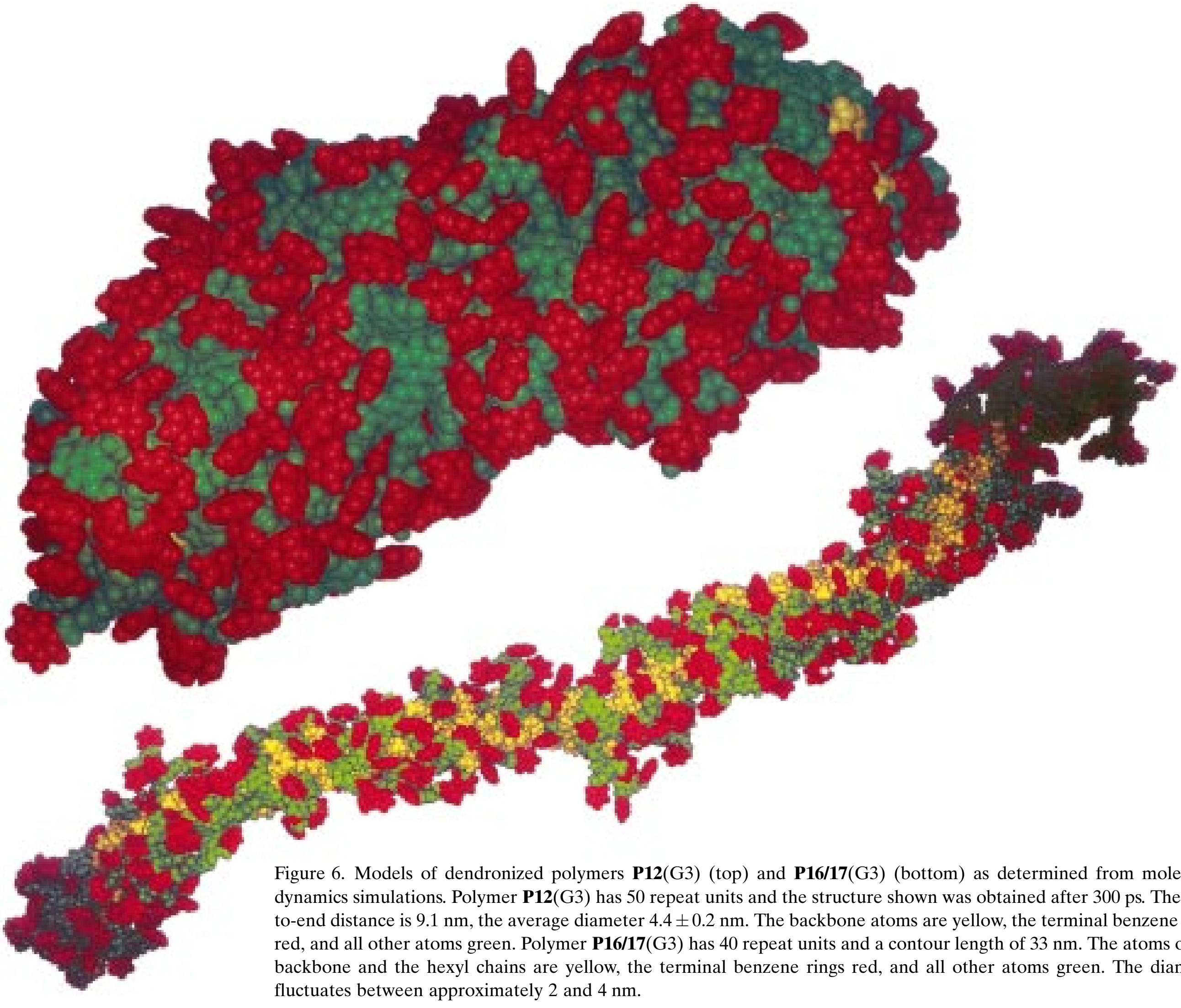


Figure 6. Models of dendronized polymers **P12**(G3) (top) and **P16/17**(G3) (bottom) as determined from molecular dynamics simulations. Polymer **P12**(G3) has 50 repeat units and the structure shown was obtained after 300 ps. The end-to-end distance is 9.1 nm, the average diameter 4.4 ± 0.2 nm. The backbone atoms are yellow, the terminal benzene rings red, and all other atoms green. Polymer **P16/17**(G3) has 40 repeat units and a contour length of 33 nm. The atoms of the backbone and the hexyl chains are yellow, the terminal benzene rings red, and all other atoms green. The diameter fluctuates between approximately 2 and 4 nm.

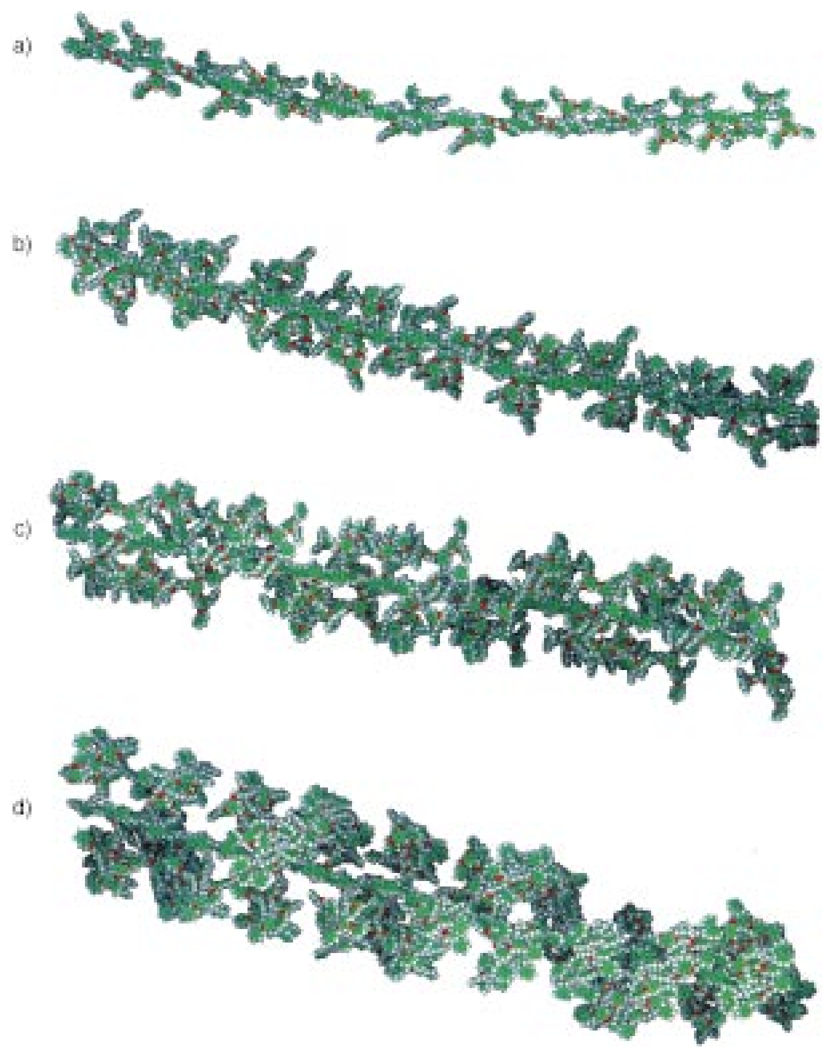
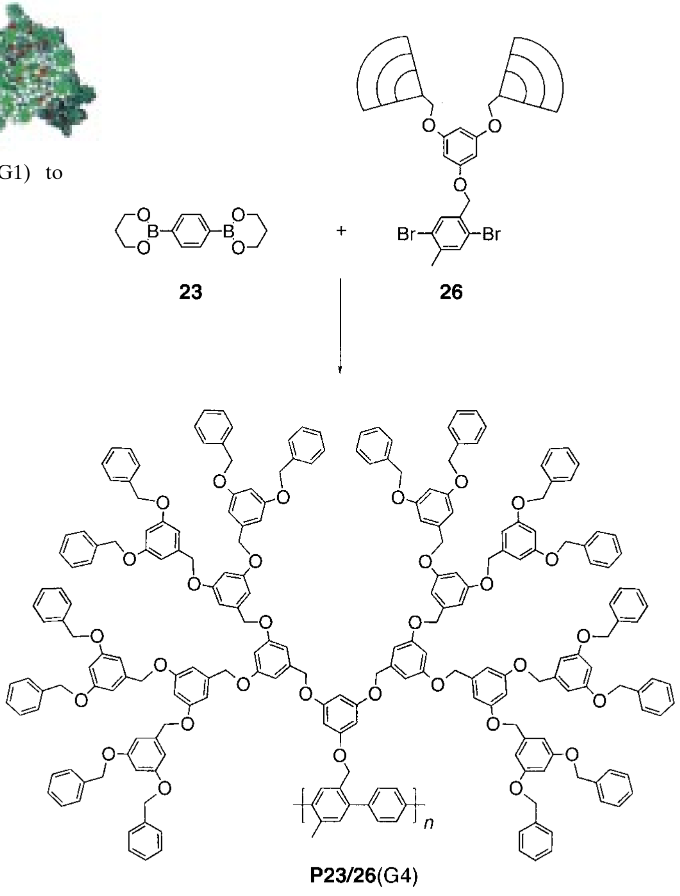


Figure 7. Computer-generated images of dendronized polymers **P16/17**(G1) to **P16/17**(G4) (a–d).

successful case.[52] The molecular weight difference between the two components **23** and **26** is so considerable (**23**: 246 g mol^{-1}; **26**: 3540 g mol^{-1}) that it was difficult to meet in practice the 1:1 stoichiometry strictly required for polycondensations. For that purpose monomer **26** was prepared on the 20-g scale. This allowed SPC on a relatively large scale, ensuring sufficient stoichiometry control. In a series of optimization experiments conditions were finally found which gave the corresponding polymer **P23/26**(G4)[53] with $P_n = 25$ and $P_w = 125$ (according to GPC) on a gram scale. Presently fractions of this material with $P_n = 10, 75, 150$, and 300 (GPC) are being investigated by SANS in order to determine their true molar mass.[54] Though it is still unclear what the actual molar mass of this polymer is, these data clearly show that SPC works even for sterically enormously loaded G4 monomers.

4. Behavior in the Bulk

The bulk properties have been investigated for polymers **P2**(G1 and G2),[22] **P4**(G2)[22] (**P2**, **P4**: $R = OC_{12}H_{25}$), and to some extent **P18/19**(G4)[41] and **P24/25**.[42] All four structures have flexible backbones with a non-compact sequence of dendrons. In the first two cases and in the last one, the dendrons have liquid crystalline properties, whereas in the third case they do not. Polymer **P2**(G1) self-assembles into a tubular supramolecular structure exhibiting enantiotropic columnar hexagonal (Θ_h) phases. These phases are characterized by differential scanning calorimetry, wide- and small-angle X-ray scattering, thermal optical polarized microscopy, and molecular modeling.[5b] The structure model proposes the stratum of the column to be formed by the backbone and the linking segments melted and segregated in the center of the column with their melted dendrons radiating towards the column periphery (Figures 8 and 9). When a second-generation dendron is used as in **P2**(G2) and **P4**(G2) an additional interesting feature is observed:[22] As the degree of polymerization increases, the dendrimer's shape shifts from spherical to cylindrical. This is accompanied by the backbone going from a random-coil to the extended conformation. This phenomenon provides the unique possibility for molecular engineering of polymer shapes, backbone conformation, and properties, and is a great way to show the interplay and impact of the above-mentioned interactions.



Scheme 2. Synthesis of **P23/26**(G4) from monomers **23** and **26** following a Suzuki polycondensation protocol.

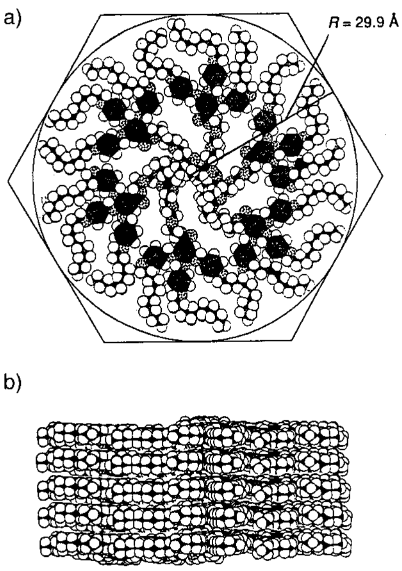


Figure 8. Schematic representation of a supramolecular cylinder of dendronized polymer **P2**(G1) ($R = OC_{12}H_{25}$, $n = 3$) in the Θ_h mesophase: a) Top view of a cylinder containing six repeat units in a stratum; the alkyl tails are melted to match the average column radius determined by X-ray scattering experiments. b) Side view of a cylinder containing 30 repeat units of the polymer assembled with melted alkyl tails. (Reproduced with permission from reference [5b].)

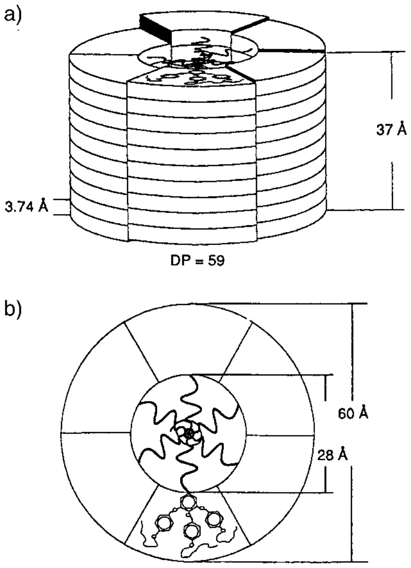


Figure 9. An idealized representation of the supramolecular cylinder formed by self-assembly from a single chain of dendronized polymer **P2**(G1) ($R = OC_{12}H_{25}$, $n = 3$) in the hexagonal columnar phase, assuming one single backbone per cylinder; drawn to proportion under consideration of existing data: a) side view; b) top view. (Reproduced with permission from reference [5b].)

Spherical and extended architectures of these dendrimers are basically proven by X-ray diffraction and can also be visualized by a scanning force microscopical (SFM) investigation using bilayers on a mica substrate.

Though polymer **P18/19**(G4) does not show any liquid crystallinity, it nevertheless forms supramolecular structures in the bulk.[40] This was concluded from X-ray diffraction patterns obtained from Si plates coated with this polymer and monomer **18**. A series of Bragg peaks for the polymer showed the existence of an ordered structure. Based on MD calculations and additional small-angle X-ray scattering experiments this structure was proposed to be body-centered cubic.

Polymer **P24/25** self-orders in solvent-cast films with the backbones parallel to the substrate and a strong solvent dependence for the degree of ordering.[41] Spacings of 22–26 Å are observed by X-ray diffraction, indicating interdigitation of the dendritic side chains. Polymer **P24/25** also forms thermotropic nematic liquid crystalline phases. With optical microscopy Schlieren textures are observed for thin films cast from solution.

5. Behavior at Solid and Fluid Interfaces

The behavior of dendronized polymers on solid substrates and at air/water interfaces is of interest from various points of views (see Section 2). One reason is that the preparation of single dendronized polymers or molecular layers thereof on solid substrates allows molecular resolution imaging by scanning force microscopy (SFM).

The behavior of the dendronized polymers at interfaces is determined not only by intra- and intermolecular forces, but also by interfacial forces.[55] The latter include a rather short-range van der Waals-type force on the nanometer scale, which is due to the different dielectric properties of the two adjacent phases. This force is always attractive, and therefore favors a high molecular segment density at the interface, which in turn favors two-dimensional crystallization since crystals exhibit usually higher densities than less ordered phases. Counteracting is the influence of entropy: Immobilizing flexible molecules in 2D crystals at interfaces reduces the entropy, since the molecules lose translational as well as conformational entropy. For the adsorption from a liquid mixture this favors the adsorption of the largest molecules, since the loss of translational entropy is counted per particle, while the van der Waals energy gained is proportional to the mass. Entropy effects also favor the adsorption of the most rigid molecules, since they lose the least conformational entropy. As a result the large and rigid rods will be preferably adsorbed from a liquid molecular mixture. In addition, there are short-range chemical forces, which are specific for the particular chemical species at the interface, and may be attractive or repulsive. Well-known consequences of these forces are epitaxial layering on crystalline substrates and the ordering of amphiphilic molecules at the air/water interface.

In the following, the behavior of two classes of dendronized polymers at interfaces will be discussed: those with one type of dendrons ("homophilic systems") and those with a hydrophobic and a hydrophilic dendron at each repeat unit ("amphiphilic systems").

5.1. Homophilic Systems

Dendronized polymers may be imaged by scanning force microscopy either in ordered ultrathin films or as individual molecules on solid supports. SFM[56, 57] is a powerful tool for investigating morphology, molecular packing, and molecular dynamics at surfaces with a resolution on the molecular scale. Examples include synthetic and biological polymers[58–60] as well as spherical dendrimers.[61, 62] Of particular interest for rather soft organic materials is the operation in the "intermittent contact" or "tapping" mode,[57] which minimizes wear during imaging.

Ultrathin layers of homophilic dendrimers can be prepared by solution casting (slow layer formation) or spin-coating (fast layer formation) from organic solvents. The SFM images of **P12**(G3) were obtained for thin (in the range of 20–30 nm) solution-casted layers on highly oriented pyrolytic graphite (HOPG, Figure 10).[50] They reveal a remarkably high degree of order: One observes domains which consist of periodic arrays of rows with a periodicity of $D = 5.0 \pm 0.5$ nm. For comparison, MD simulations (Figure 6, top) and SANS measurements reveal rod diameters of $D = 4.4 \pm 0.2$ nm and $D = 5.1 \pm 0.5$ nm, respectively. These numbers are very similar to the distances between the rows, suggesting that the rows can be attributed to molecules which are predominantly oriented parallel to the surface. They are grouped in anisotropic domains whose sizes vary between 20 and 200 nm (parallel to the director axis) and 20 and 100 nm (perpendicular to the director axis). A reliable correlation of individual chain lengths with domain size is not possible. Despite the high resolution of the image, only the chain ends at the grain boundaries can be clearly identified. In contrast, those in the interior may be obscured if two dendrimers with the same director axis are in tight contact and oscillate somewhat along this axis.[50] Large-scale SFM images show that the films exhibit terraces with height differences Δh between adjacent terraces of 4.2 ± 0.2 nm. This is close to $5.0\ \text{nm} \cos 30^\circ = 4.3$ nm, which one would expect for a model of close-packed cylinders with a diameter of 5 nm (Figure 11).

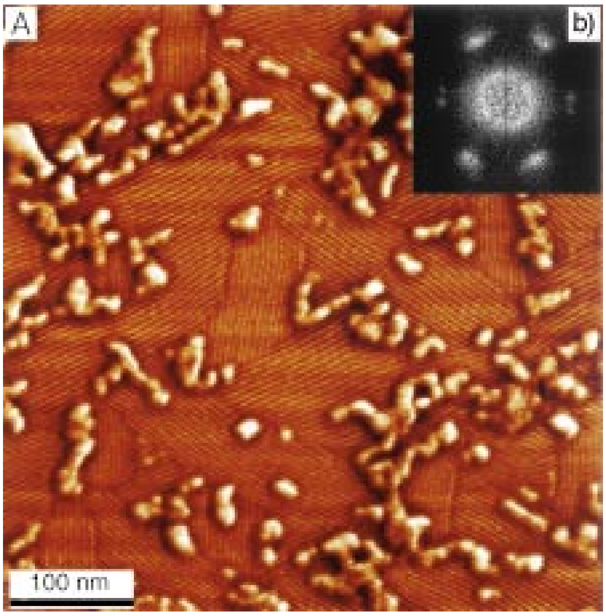


Figure 10. a) Phase-contrast SFM image (tapping-mode) of an ultrathin layer of **P12**(G3) on HOPG.[50] The rows are attributed to molecules which are predominantly oriented parallel to the surface as well as to each other. Their orientation within the surface plane also reflects the threefold symmetry of the substrate, as indicated by the Fourier transform (b).

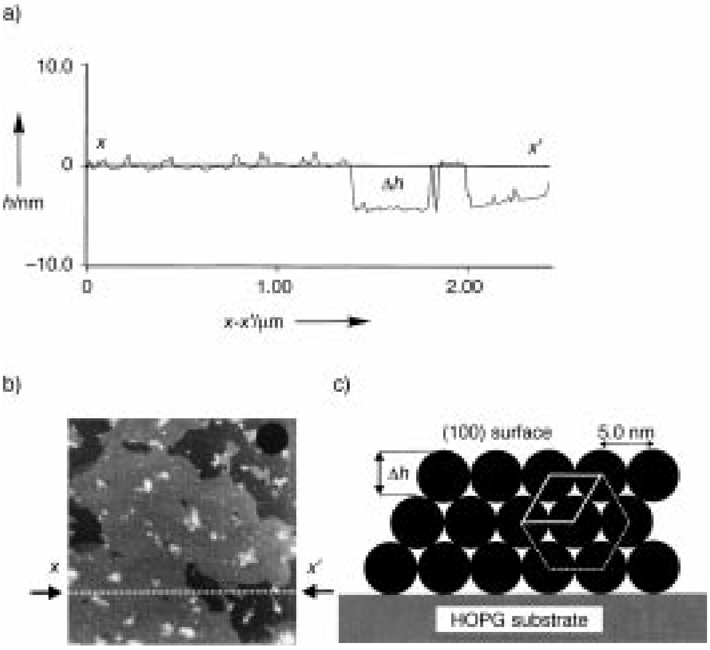


Figure 11. Some SFM results of ultrathin films of **P12**(G3) on HOPG and a packing model.[50] a) Cross-sectional profile along $x-x'$ as indicated in b). The height difference between adjacent terraces has the dimension of a monolayer ($\Delta h = 4.2 \pm 0.2$ nm). b) Large-scale SFM image ($2.4 \times 2.4\ \mu m^2$) of molecular terraces. c) Schematic model of close-packed molecularly defined cylinders. See text for further details.

Interestingly, the different domains in Figure 10 exhibit three molecular orientations at 60 ± 8° relative to each other, indicating that even in a layer with a thickness of about five monolayers the top layer reflects the threefold symmetry of the graphite substrate. While this symmetry is stable with time, reorientations by 120° do occur. For the case of a similar polymeric dendrimer, **P16/17**(G3), this is demonstrated in Figure 12.[51]

These results show that the ultrathin layers of the described dendronized polymers offer the possibility to orient the polymeric backbones along the substrate axes, and to access molecular dimensions in arrays by SFM imaging. To determine the properties of single molecules, such as persistence lengths or Young's or bending moduli, it is desirable to prepare submonolayers with isolated single molecules on the surface. A convenient preparation for this is spin-coating HOPG from a dilute solution. The SFM images of **P2**(G1) (Figure 13)[63] reveal single molecules stretched out on the surface with sharp kinks of typically 120°, which then reflect the symmetry of the substrate. The sharpness of the kinks indicates that this polymer is quite flexible. The SFM images may also be used to determine the distributions of contour lengths. They revealed that **P2**(G1)—that is, a polymer with a side group that is not very spatially demanding—appeared to be at least two times shorter than the contour length expected on the basis of size-exclusion chromatography and static light scattering. This was attributed to a disordered helixlike conformation of the polymeric backbone, and can be con-

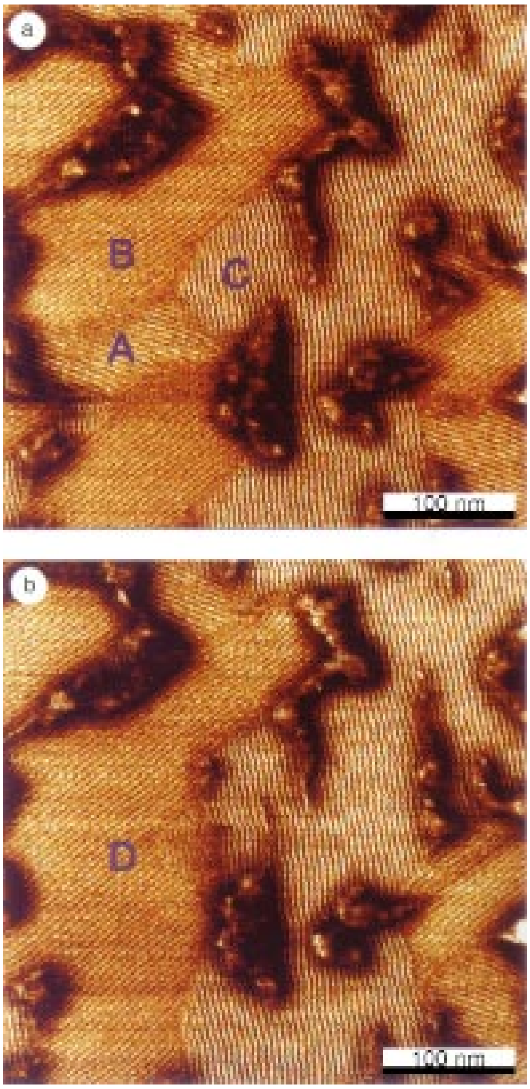


Figure 12. Phase-contrast SFM images (tapping-mode) of an ultrathin film of **P16/17**(G3) on HOPG.[51] The rows are attributed to molecules which are predominantly oriented parallel to the surface as well as to each other. Their orientation within the surface plane also reflects the threefold symmetry of the substrate (three molecular orientations denoted A, B, and C in a)). Images a) and b) were recorded at the same position at an interval of 10 min. Domain A reorients in the same direction as domain B, resulting in a new domain D.

trasted to the case of **P4**(G1) with a spatially more demanding side group, whose contour lengths agreed fairly well with the expectation.[63] This shows that bulky dendrons force the backbone into extension and that there is a degree of freedom for less bulky dendrons, namely, the conformation of the flexible polymer backbone, which may be used to control the contour length of the dendronized polymer (e.g., by contraction through helix formation).

Another means to stiffen a polymer is by Coulombic charges along the backbone. Whereas **P11**(G1) is quite flexible (Figure 14a), the corresponding positively charged derivative without the trimethylsilylethylenoxycarbonyl (Teoc) protecting group is rather stiff (Figure 14b).[65] The latter polymers are therefore, similar to the polymers with bulky dendrons **P12**(G3) and **P16/17**(G4), suitable candidates for one-by-one manipulation with the SFM tip, just like rolling trees on the ground.

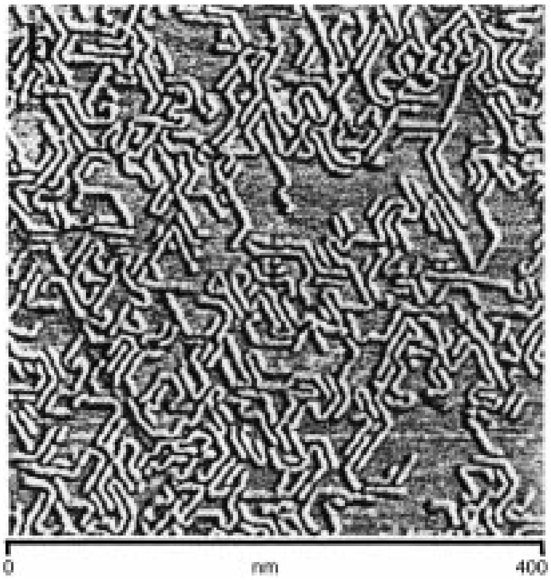


Figure 13. SFM image (tapping-mode) of **P2**(G1) on HOPG.[63] It shows that the molecular orientations reflect the symmetry of the substrate, and that the molecules are flexible enough to be frequently bent by 120°. The strong tendency for the single molecule to align along lattice axes of the substrate has been attributed to the orientation of the pendant alkyl chains.[63, 64]

Another example for the manipulation of dendronized polymers with the SFM is shown in Figure 15, which was obtained as follows: First about one monolayer of a rather low molecular weight fraction (on the order of ten monomers on average according to GPC with polystyrene standard) of **P16/17**(G4) was spin-coated on HOPG. The result is an apparently disordered surface. Scanning with the SFM-tip, however, orients the molecules almost prefectly uniformly in the whole scan window, which can be 1 μm^2 or more, and is limited apparently only by the domain size of the underlying HOPG, which is typically on the order of 10 μm but also varies.

5.2. Amphiphilic Systems

Amphiphilic dendronized polymers may lead to amphiphilic cylinders which, depending on the surrounding medium, could segregate lengthwise into two different halves (Figure 16). This structural motif is rather unique. In nature it can be found in some ion channel membrane proteins, which means that amphiphilically dendronized polymers are of interest as models for such proteins.[66–68] They may also serve as novel and giant constituents of self-aggregated assemblies and should show interesting behavior at interfaces. A good candidate is a dendronized polymer whose repeating units are equipped with two sterically demanding substituents, one hydrophobic and the other hydrophilic.[69] This area was entered with the three differently equipped poly(*para*-phenylene)s **P20/23**, **P21/23**, and **P22/23**, which differ in the relative spatial demand of their polar and nonpolar substituents (Figure 16).

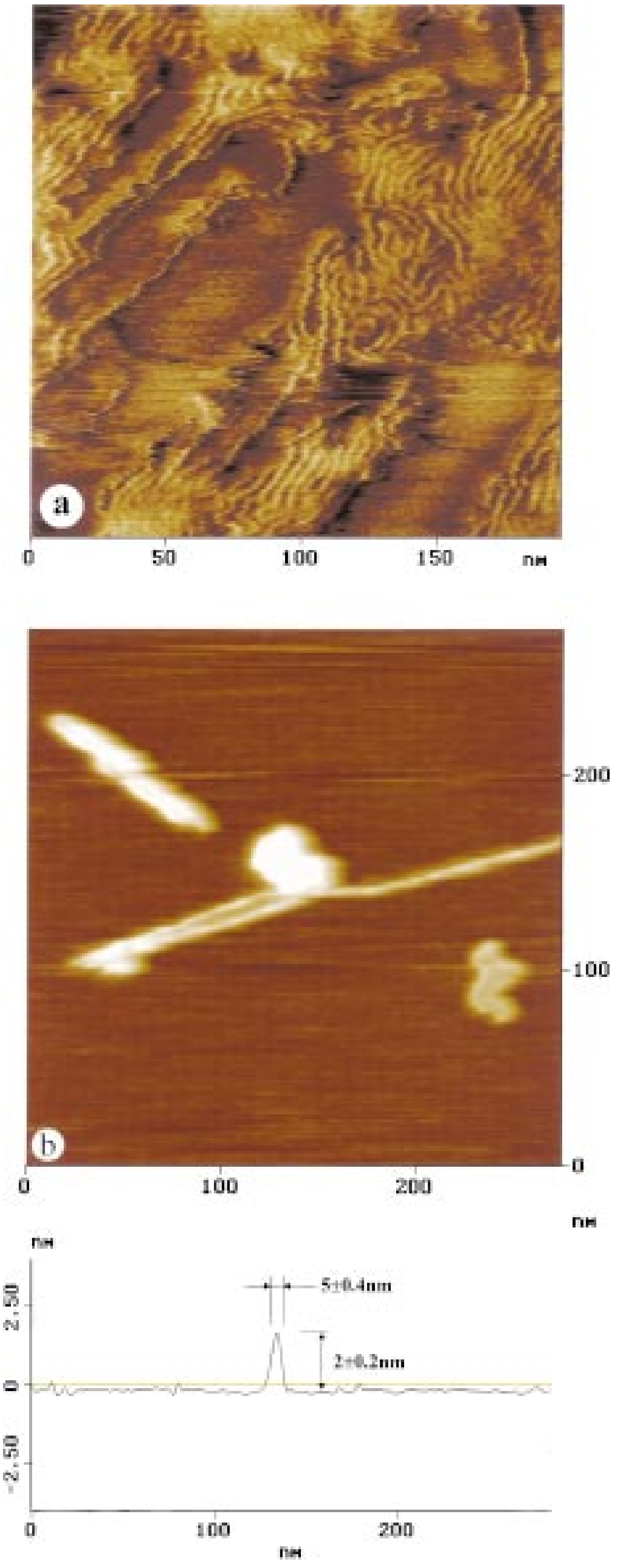


Figure 14. SFM images (tapping-mode) of two low-generation dendronized polymers: a) **P11**(G1) (phase image: 0–30°) and b) its unprotected and quaternized (charged) counterpart on HOPG (height image: 0–8 nm).[65] Whereas the neutral **P11**(G1) is rather flexible, as evidenced also by the fact that the exact conformation changes on the time scale of the measurement, the charged species appears very rigid, as judged by the straightness of the feature going from left to right over more than 200 nm. The two kinks in this feature may indicate that it consists of several individual rods that are roughly 100 nm long. The height profile was taken perpendicular to the *x* axis at 200 nm.

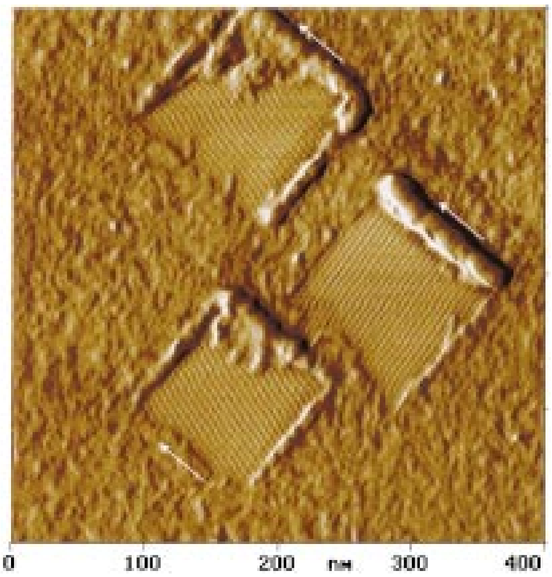


Figure 15. Phase-contrast SFM image (tapping-mode) of a monolayer of oligomeric **P23/26**(G4) after scanning of three areas.[65] It reveals that upon scanning the molecules are perfectly oriented along one of the three symmetry axes of the substrate.

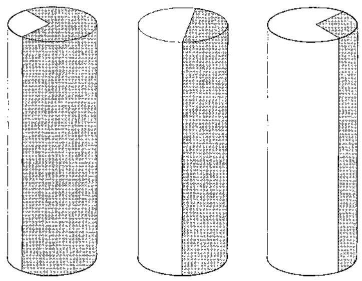


Figure 16. Cartoon representations of (not yet fully realized) amphiphilically equipped dendritic cylinders with varying spatial demands of polar and nonpolar domains. The lengthwise segregation of these domains is interesting for surface modifications and for attaining unprecedented aggregates in solution.

There are different ways to prepare ultrathin layers from amphiphilic polymers: One method is to form Langmuir monolayers at the air/water interface followed by transfer to solid substrates using the Langmuir–Blodgett technique. Another way is spin-coating, as for the homophilic systems.

5.2.1. Langmuir and Langmuir–Blodgett (LB) layers

Molecules based on amphiphilic dendrons have been investigated at the air/water interface, and stable monolayers were found for some of these systems.[70] In a recent, elegant study by Frank and Hawker et al.[71] the behavior of hydrophobic Fréchet-type dendrons carrying hydrophilic ethyleneoxy (EO) chains at their focal point was studied at this interface by systematically varying the dendron size (G3 to G5) and chain length. Longer hydrophilic chains increased the stability of the Langmuir films for G3 and G4 by roughly 3.1 and 4.1 $\mathrm{mN\,m^{-1}}$, respectively, per additional EO unit. On going from the lower to the higher generations the shape of the dendrons changes from vertically elongated to more flat.

The collapse pressures ranged from approximately 6 mN m^{-1} for G3 with one EO group to 25 mN m^{-1} for G3 with six EO groups.

Langmuir monolayers of monomer **20** and polymer **P20/23** have been prepared at the air/water interface.[38] The surface pressure–area isotherms exhibited at room temperature reveal stable monolayers. The monolayers of **20** display very good reversibility for compression, decompression, and repeating cycles, with an area of about 0.73 nm^2 per molecule at 20 mN m^{-1}. These data are consistent with a monolayer structure in which the four EO chains per water-soluble dendron are close packed and oriented perpendicular to the monolayer, thereby defining a minimum area per molecule. In comparison, polymer **P20/23** exhibits a 10% larger area per RU (0.82 nm^2 RU^{-1}) upon the first compression with a hysteresis in the first decompression and a shift to a more reversible isotherm and a smaller area per RU in the second cycle (0.77 nm^2 RU^{-1}). The good agreement between the areas per molecule for monomer **20** and the per repeat unit of polymer **P20/23** indicates a structure for the polymer monolayer in which the rodlike polymer molecules are oriented with their long axes within the monolayer plane and close-packed. Moreover, the hydrophylic EO chains are on the side of the polymer that faces the water subphase, while the more hydrophobic dendron faces the air side of the polymer. This picture is supported by a control experiment with a closely related polymer in which the hydrophilic dendron of **P20/23** is replaced by another G2 Fréchet dendron (structure not shown). Under the same conditions this polymer does not form a stable monolayer at the air/water interface.

Polymers **P21/23** and **P22/23** and the corresponding monomers **21** and **22** were also investigated at the air/water interface.[39] With the exception of **P22/23** they all form stable monolayers on the Langmuir trough, which can be transfered by the Langmuir–Blodgett technique to mica. Whereas the transfered films of **21** and **22** are unstable, **P21/23** forms stable, rather smooth monolayers whose morphology remains unchanged for at least a week. The fact that both monomers are stable on water but not on mica reflects the discrepancy of the spatial demand of the hydrophilic and hydrophobic parts. Since the polymer **P21/23** is stable on mica, the covalent attachment of the amphiphilic repeat units can stabilize an LB layer. On the other hand, the fact that **P22/23** does not form a stable monolayer, not even on water, indicates that this polymer, with its amphiphilic imbalance, does not behave like an amphiphile under these conditions.

A quantitiative comparison of the collapse pressures of the Curtis–Hawker amphiphiles[71] with the ones described here cannot be made. There are substantial structural differences, even if this comparison is restricted to the monomers **20**–**22**. Additionally the Curtis–Hawker amphiphiles have EO chains with terminal (polar) hydroxy functionalities, whereas the monomers have (unpolar) methoxy groups. The collapse pressures are, however, in a similar range.

Usually, no SFM images with molecular-scale resolution were obtained for the LB layers, in contrast to the case of the analogous homophilic systems preparared by spin-coating. Therefore spin-coating has been employed as an alternative preparation method also for the amphiphilic systems.[65] Figure 17 displays an SFM image of a spin-coat monolayer of **P20/23** on HOPG, which reveals rather straight rods. Again, their orientation within the plane is not random, but it reflects the threefold symmetry of the substrate. Within experimental error, the length distribution of the rods agrees with the values determined by size-exclusion chromatography. However, the distance between the rods is 4.4 ± 0.5 nm, which is larger than one would expect for close-packed molecules. A possible explanation is a well-defined aggregation of the amphiphilic rods, for example into dimers which exhibit hydrophobic surfaces that are in contact with both the rather hydrophobic substrate and the ambient.

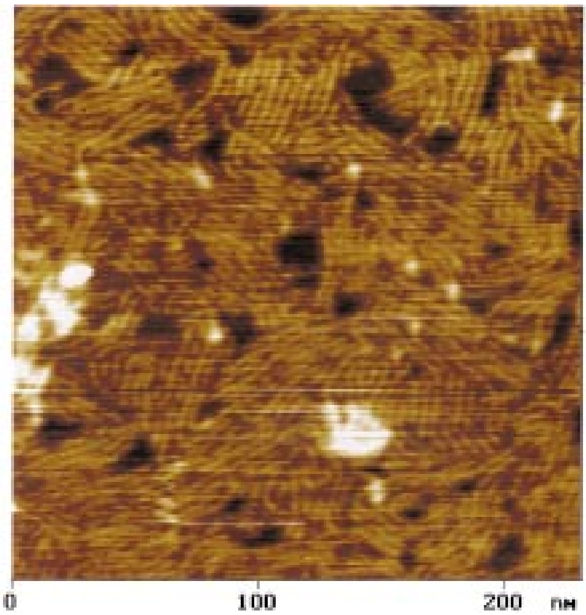


Figure 17. Molecular-resolution SFM height image of spin-coated amphiphiles **P20/23** on HOPG.[65]

6. Modification of Cylinder "Surfaces"

Controlled surface modification of dendritic nanorods is a challenging goal for both synthesis and many application-related issues. Some initial experiments have already been undertaken. The essential steps are:

a) Synthesis of monomers with protected functional groups in the periphery. The protection is required for compatibility with the polymerization conditions.
b) Polymerization of these monomers and complete deprotection of the peripheral functional groups of the resulting polymer. The resulting deprotected polymer needs to be soluble.
c) Derivatization of the deprotected polymer with the desired groups or functional units.

Step a has been solved for at least up to generation two. Monomers **7**, **8**, **10**, and **11** in Figure 2 are good examples of this. These monomers have all been polymerized to the corresponding high molar mass materials **P7**, **P8**, **P10**, and **P11** (step b) and their functional groups deprotected. For the use of the somewhat uncommon Teoc protecting group, see reference [25]. Figure 18 shows ^{1}H NMR spectra of monomer **7**(G2), the corresponding polymer **P7**(G2), and its deprotected counterpart. The deprotection can obviously be driven to completion. This is important because remaining protected functional groups are an integral part of the polymer and cannot be removed by purification as in common organic chemistry. Step c is the least developed. Scheme 3 shows a synthetic sequence in which the deprotected G1 polymer **P11**(G1) is allowed to react at the amine groups with the active ester of the protected G1 dendron **27** to give polymer **P8**(G2). The structure of this polymer was proven by all common means and additionally by independent preparation from monomer **8**(G2).[29] Comparison of the ^{1}H NMR spectra (500 MHz) of samples obtained from the two routes proves that the coverage with **27** is virtually complete. This result is nice, but the chemistry is certainly not yet where it should be. The starting material was just a G1 polymer, which is anything else but a cylindrically shaped nanoobject, even if one takes the stiffening effect caused by the two positive charges of the ammonium functionalities into consideration. It is positive, however, that a polymer with roughly $P_n = 80-100$, which translates into 160–200 amine groups, could be completely covered with G1 dendrons. This experiment has initiated studies of more complex systems.

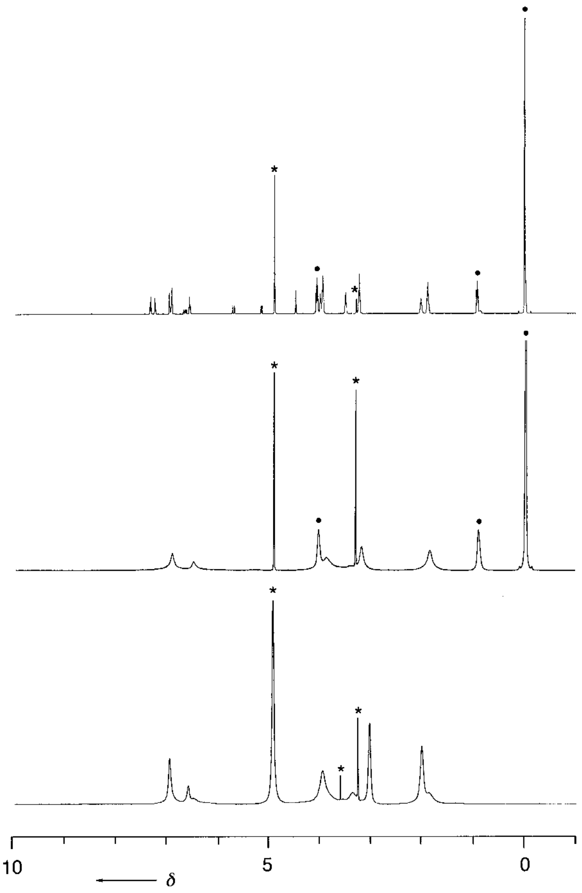
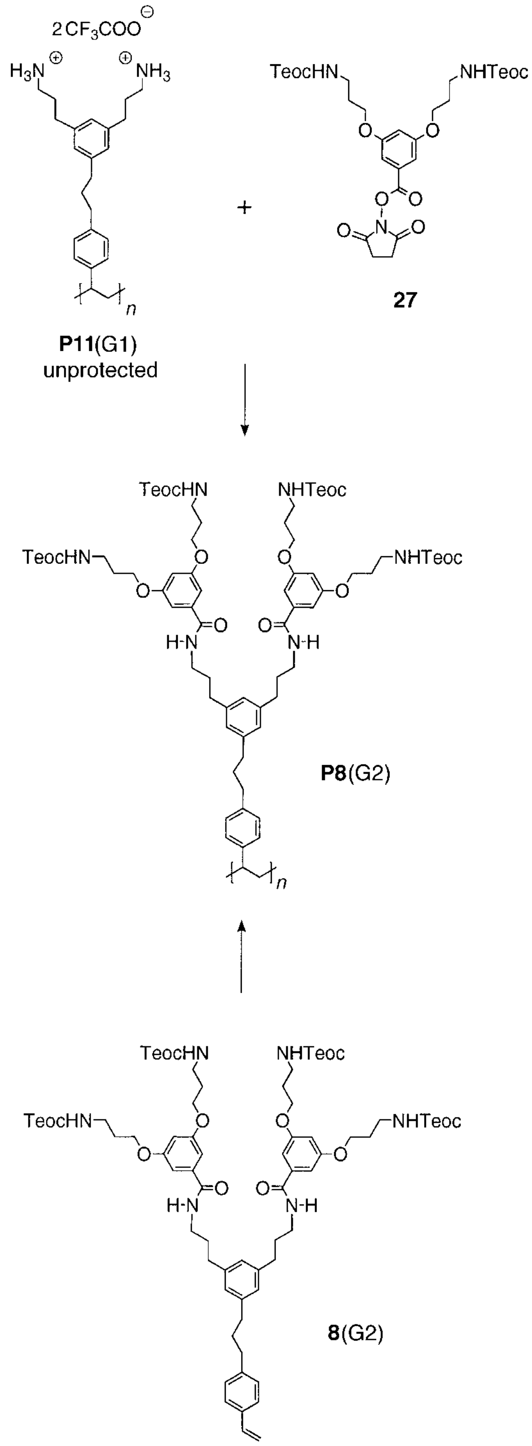


Figure 18. The ^{1}H NMR spectra of monomer **7**(G2), the corresponding polymer **P7**(G2), and its deprotected counterpart (from top to bottom) illustrate the structure control during polymerization and the degree to which deprotection of the polymer can be achieved. The signals of the Teoc protecting group (●) and the solvent (*) are marked.



Scheme 3. Two different synthetic routes to polymer **P8**(G2) starting from **P11**(G1) with subsequent dendronization or from macromonomer **8**(G2).

Attachment under amide formation was selected because it allows easy use of almost any interesting component—such as amino acids, sugars, or short DNAs—instead of dendrons. An alternative way to get to modified dendronized polymers is to polymerize modified dendronized monomers. For example, monomers **9**(G1 and G2) give sugar-coated polymers **P9**.[28]

7. Summary and Outlook

High molecular weight dendronized polymers are synthetically accessible. If certain prerequisites are taken into account, even the sterically demanding macromonomers **12**(G3), **16**(G3), and **26**(G4) can be employed, which widens the scope of both radically initiated polymerizations as well as Suzuki polycondensations. The successful synthesis of polymers such as **P12**(G3) and **P23/26**(G4) allows investigation of the impact of the dendritic decoration on the backbones' coiling behavior and addresses the important question of whether or not steric congestion can be used as a tool to force molecules into a certain shape, which is more or less independent of the surrounding medium (in solution, adsorbed on surfaces, spread at solid/liquid interfaces, and in the solid state). SFM and SANS measurements as well as MD simulations reveal that, for example, polymer **P12**(G3) is remarkably stiff and can be viewed as a cylindrically shaped molecular object with a defined diameter of approximately 5 nm and a persistance length on the order of the contour length (50 nm). One may even be inclined to assign a "surface" to this polymer. Driven by the idea of generating molecular nanoobjects with functional surfaces just by polymerizing appropriately equipped monomers, researchers made the first steps to decorate these surfaces with both functional and polar/unpolar groups in order to engineer properties and explore possible fields of application.

Research on nanoobjects of the kind described is a truly interdisciplinary enterprise, and progress depends upon tight cooperation between synthetic chemists, experimental physicists, and theoreticians. Some future directions will be a) to develop synthesis to the point where several rigid objects with various surface functionalities are available and their lengths distributions are somewhat better under control, b) to isolate individual cylinders on surfaces and determine quantitatively molecular properties such as bending moduli, c) to try to move these objects about on surfaces for patterning and construction purposes, and d) to start investigations into their properties along the lines described in Section 2.

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[1] G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendritic Molecules—Concepts, Syntheses, Perspectives*, VCH, Weinheim, **1996**; see also, for example, D. K. Smith, F. Diederich, *Chem. Eur. J.* **1998**, *4*, 1353–13621; H. Frey, C. Lach, K. Lorenz, *Adv. Mater.* **1999**, *10*, 279–294; C. Gorman, *Adv. Mater.* **1999**, *10*, 295–309; A. W. Bosman, H. M. Janssen, E. W. Meijer, *Chem. Rev.* **1999**, *99*, 1665–1688.

[2] J. F. G. A. Jansen, E. M. M. de Brabander-van den Berg, E. W. Meijer, *Science* **1994**, *266*, 1226–1229; J. F. G. A. Jansen, E. W. Meijer, E. M. M. de Brabander-van den Berg, *J. Am. Chem. Soc.* **1995**, *117*, 4417–4428.

[3] D. A. Tomalia, H. Baker, J. R. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder, P. Smith, *Polym. J. (Tokyo)* **1985**, *17*, 117–132; D. A. Tomalia, H. Baker, J. R. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder, P. Smith, *Macromolecules* **1986**, *19*, 2466–2468; E. M. M. de Brabander-van den Berg, E. W. Meijer, *Angew. Chem.* **1993**, *105*, 1370–1372; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1308–1310; C. Wörner, R. Mülhaupt, *Angew. Chem.* **1993**, *105*, 1367–1370; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1306–1308.

[4] D. A. Tomalia, P. M. Kirchhoff (Dow Chemical), US-A 4694064, **1987**; R. Yin, Y. Zhu, D. A. Tomalia, H. Ibuki, *J. Am. Chem. Soc.* **1998**, *120*, 2678–2679.

[5] a) A. D. Schlüter, presented at The Polymer Conference, Cambridge, UK, **1993**; R. Freudenberger, W. Claussen, A. D. Schlüter, H. Wallmeier, *Polymer* **1994**, *35*, 4496–4501; b) V. Percec, J. Heck, D. Tomazos, F. Falkenberg, H. Blackwell, G. Ungar, *J. Chem. Soc. Perkin Trans.* **1993**, 2799–2811.

[6] For an excellent report on the structural perfection of dendrimers, see J. C. Hummelen, J. L. J. van Dongen, E. W. Meijer, *Chem. Eur. J.* **1997**, *3*, 1489–1493.

[7] I. Gitsov, K. L. Wooley, J. M. J. Fréchet, *Angew. Chem.* **1992**, *104*, 1282–1285; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1200–1203; I. Gitsov, J. M. J. Fréchet, *Macromolecules* **1993**, *27*, 7309–7314; C. J. Hawker, J. M. J. Fréchet, *Polymer* **1992**, *33*, 1507–1510; T. Kawaguchi, J. S. Moore, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **1994**, *35*, 872–873; M. A. Fox, *Chem. Mater.* **1998**, *10*, 860–863.

[8] M. L. Bruening, Y. Zhou, G. Aguilar, R. Agee, D. E. Bergbreiter, R. M. Crooks, *Langmuir* **1997**, *13*, 770–778; Z. Bo, L. Zhang, B. Zhao, X. Zhang, J. Shen, S. Höppener, L. Chi, H. Fuche, *Chem. Lett.* **1998**, 1197–1198; L. Zhang, Z. Bo, B. Zhao, Y. Wu, X. Zhang, J. Shen, *Thin Solid Films* **1998**, 327–329, 221–223; R. F. Peez, D. L. Dermody, J. G. Franchina, S. J. Jones, M. L. Bruening, D. E. Bergbreiter, R. M. Crooks, *Langmuir* **1998**, *14*, 4232–4237.

[9] See, for example, M. Fischer, F. Vögtle, *Angew. Chem.* **1999**, *111*, 934–955; *Angew. Chem. Int. Ed.* **1999**, *38*, 884–905.

[10] H. Frey, *Angew. Chem.* **1998**, *110*, 2313–2317; *Angew. Chem. Int. Ed.* **1998**, *37*, 2193–2197.

[11] A. D. Schlüter, *Top. Curr. Chem.* **1998**, *197*, 165–191.

[12] P. Dziezok, S. S. Sheiko, K. Fischer, M. Schmidt, M. Möller, *Angew. Chem.* **1997**, *109*, 2894–2897; *Angew. Chem. Int. Ed. Engl* **1997**, *36*, 2812–2815; S. S. Sheiko, M. Gerle, K. Fischer, M. Schmidt, M. Möller, *Langmuir* **1997**, *13*, 5368–5372; M. Gerle, K. Fischer, S. Roos, A. H. E. Müller, M. Schmidt, S. S. Sheiko, S. Prokhorova, M. Möller, *Macromolecules* **1999**, *32*, 2629–2634; R. Djalali, N. Hugenberg, K. Fischer, M. Schmidt, *Macromol. Rapid Commun.* **1999**, *20*, 444–449.

[13] H.-G. Elias, *Makromoleküle*, 5. Aufl., Hüthig&Wepf, Basel, **1990**, S. 43, 628.

[14] For discussions on the density gradient in spherically shaped dendrimers, see R. G. deGennes, H. J. Hervet, *Phys. Lett. Paris* **1983**, *44*, 351–359; R. L. Lescanec, M. Muthukumar, *Macromolecules* **1990**, *23*, 2280–2288.

[15] J. W. J. Knappen, A. W. van der Made, J. C. de Wilde, P. W. N. M. van Leeuwen, P. Wijkens, D. M. Grove, G. van Koten, *Nature* **1994**, *372*, 659–662; N. Brinkmann, D. Giebel, G. Lohmer, M. T. Reetz, U. Kragl, *J. Catal.* **1999**, *183*, 163–168; N. J. Hovestad, E. B. Eggeling, H. J. Heidbuechel, J. T. B. H. Jastrzebski, U. Kragl, W. Keim, D. Vogt, G. van Koten, *Angew. Chem.* **1999**, *111*, 1763–1765, *Angew. Chem. Int. Ed.* **1999**, *38*, 1655–1658.

[16] H. Maeda, *Langmuir* **1997**, *13*, 4150–4161, and references therein.

[17] "Molecular Assemblies and Membranes": J.-H. Fuhrhop, J. Köning in *Supramolecular Chemistry* (Ed.: J. F. Stoddart), Royal Society of Chemistry, London, **1994**.

[18] W. W. Yan, J. J. Kirkland, D. D. Bly, *Modern Size-Exclusion Chromatography*, Wiley, New York, **1979**.

[19] J. M. J. Fréchet, K. L. Wooley, C. J. Hawker, *J. Am. Chem. Soc.* **1991**, *113*, 4252–4261.

[20] The authors refer to compound **2** as a monomer with tapered side chains. Since the side chains meet the criteria for a G1 dendron, compound **2** is considered here.

[21] G. Draheim, H. Ritter, *Macromol. Chem. Phys.* **1995**, *196*, 2211 – 2222.

[22] V. Percec, C. H. Ahn, G. Ungar, D. J. P. Yeardley, M. Möller, S. S. Sheiko, *Nature* **1998**, *391*, 161 – 164.

[23] Y. M. Chen, C. F. Chen, W. H. Liu, F. Xi, *Macromol. Rapid Commun.* **1996**, *17*, 401 – 407.

[24] I. Neubert, R. Klopsch, W. Claussen, A. D. Schlüter, *Acta Polym.* **1996**, *47*, 455 – 459.

[25] I. Neubert, A. D. Schlüter, *Macromolecules* **1998**, *31*, 9372 – 9378.

[26] For a related O-terminated dendron, see ref. [19].

[27] L. Shu, A. D. Schlüter, *Macromol. Chem. Phys.* **2000**, *201*, 239 – 245.

[28] A. Zistler, S. Koch, A. D. Schlüter, *J. Chem. Soc. Perkin Trans. 1* **1999**, 501 – 508.

[29] L. Shu, A. D. Schlüter, unpublished results.

[30] I. Neubert, E. Amoulong-Kirstein, A. D. Schlüter, *Macromol. Rapid Commun.* **1996**, *17*, 517 – 527.

[31] T. Kaneko, T. Horie, M. Asano, T. Aiko, E. Oikawa, *Macromolecules* **1997**, *30*, 3118 – 3121.

[32] K. J. Ivin, *Olefin Metathesis*, Academic Press, London, **1983**.

[33] V. Percec, D. Schlueter, J. C. Ronda, G. Johansson, G. Ungar, J. P. Zhou, *Macromolecules* **1996**, *29*, 1464 – 1472.

[34] V. Percec, D. Schlueter, *Macromolecules* **1997**, *30*, 5783 – 5790.

[35] A. D. Schlüter, G. Wegner, *Acta Polymer.* **1993**, *44*, 59 – 69.

[36] W. Claussen, N. Schulte, A. D. Schlüter, *Macromol. Rapid Commun.* **1995**, *16*, 89 – 94.

[37] B. Karakaya, W. Claussen, K. Gessler, W. Saenger, A. D. Schlüter, *J. Am. Chem. Soc.* **1997**, *119*, 3296 – 3301.

[38] Z. Bo, J. P. Rabe, A. D. Schlüter, *Angew. Chem.* **1999**, *111*, 2540 – 2542, *Angew. Chem. Int. Ed.* **1999**, *38*, 2370 – 2372.

[39] Z. Bo, C. Zhang, N. Severin, J. P. Rabe, A. D. Schlüter, *Macromolecules* **2000**, in press.

[40] S. Jahromi, B. Coussens, N. Meijerink, A. W. M. Braam, *J. Am. Chem. Soc.* **1998**, *120*, 9753 – 9762.

[41] Z. Bao, K. R. Amundson, A. J. Lovinger, *Macromolecules* **1998**, *31*, 8647 – 8649.

[42] A. P. H. J. Schenning, R. E. Martin, M. Ito, F. Diederich, C. Boudon, J.-P. Gisselbrecht, M. Gross, *Chem. Commun.* **1998**, 1013 – 1014.

[43] V. Hensel, A. D. Schlüter, *Liebigs Ann.* **1997**, 303 – 309.

[44] Y. Tsukahara, K. Tsutsumi, Y. Yamashita, S. Shimada, *Macromolecules* **1990**, *23*, 5201 – 5208; M. Wintermantel, M. Gerle, K. Fischer, M. Schmidt, I. Wataoka, H. Urakawa, K. Kajiwara, Y. Tsukahara, *Macromolecules* **1996**, *29*, 978 – 983.

[45] M. Schmidt, Mainz, personal communication.

[46] V. Percec, C.-H. Ahn, B. Barboin, *J. Am. Chem. Soc.* **1997**, *119*, 12 978 – 12 979.

[47] K. Ito, S. Kawaguchi, *Adv. Polym. Sci.* **1999**, 129 – 178.

[48] S. Förster, I. Neubert, A. D. Schlüter, P. Lindner, *Macromolecules* **1999**, *32*, 4042 – 4049.

[49] J. M. G. Cowie, *Polymers: Chemistry & Physics of Modern Materials*, International Textbook Comp., Bucks, UK, **1973**.

[50] W. Stocker, B. L. Schürmann, J. P. Rabe, S. Förster, P. Lindner, I. Neubert, A. D. Schlüter, *Adv. Mater.* **1998**, *10*, 793 – 797.

[51] W. Stocker, B. Karakaya, B. L. Schürmann, J. P. Rabe, A. D. Schlüter, *J. Am. Chem. Soc.* **1998**, *120*, 7691 – 7695.

[52] Z. Bo, A. D. Schlüter, *Macromol. Rapid Commun.* **1999**, *20*, 21 – 25; Z. Bo, A. D.Schlüter, *Chem. Eur. J.* **2000**, in press.

[53] The dendron of **P23/26**(G4) is not exactly of the Fréchet-type. For improved synthetic availability the first branching unit was modified.

[54] S. Förster, Z. Bo, A. D. Schlüter, unpublished results.

[55] J. N. Israelachvili: *Intermolecular and Surface Forces*, Academic Press, London, **1985**.

[56] G. Binnig, C. F. Quate, C. Gerber, *Phys. Rev. Lett.* **1986**, *56*, 930.

[57] Q. Zhong, D. Innis, V. Elings, *Surf. Sci.* **1993**, *290*, 688.

[58] H. G. Hansma, J. Vesenka, C. Siegerist, G. Kelderman, H. Morret, R. L. Sinsheimer, V. Elings, C. Bustamate, P. K. Hansma, *Science* **1992**, *256*, 1180.

[59] H. G. Hansma, F. Motademi, P. Smith, P. K. Hansma, J. C. Wittmann, *Polymer* **1992**, *33*, 674.

[60] S. J. Tans, L. J. Geerlings, C. Dekker, J. Wu, G. Wegner, *Synth. Met.* **1997**, *84*, 733.

[61] S. S. Sheiko, G. Eckert, G. Ignat'eva, A. M. Muzafarov, J. Spickermann, H. J. Räder, M. Möller, *Macromol. Rapid Commun.* **1996**, *17*, 283; S. S. Sheiko, A. M. Muzafarov, R. G. Winkler, E. V. Getmanova, G. Eckert, P. Reineker, *Langmuir* **1997**, *13*, 4172.

[62] M. C. Coen, K. Lorenz, J. Kressler, H. Frey, R. Mülhaupt, *Macromolecules* **1996**, *29*, 8069.

[63] S. A. Prokhorova, S. S. Sheiko, M. Möller, C.-H. Ahn, V. Percec, *Macromol. Rapid Commun.* **1998**, *19*, 359 – 366; S. A. Prokhorova, S. S. Sheiko, C.-H. Ahn, V. Percec, M. Möller, *Macromolecules* **1999**, *32*, 2653 – 2660.

[64] J. P. Rabe, S. Buchholz, *Science* **1991**, *253*, 424 – 427.

[65] J. Barner, Diplomarbeit, Humboldt-Universität Berlin, **1999**.

[66] N. Voyer, J. Lamothe, *Tetrahedron* **1995**, *51*, 9241; N. Voyer, M. Robitaille, *J. Am. Chem. Soc.* **1995**, *117*, 6599.

[67] For amphiphilic spherical dendrimers, see F. Zeng, S. C. Zimmermann, *Chem. Rev.* **1997**, *97*, 1681 – 1712; A. P. H. J. Schenning, C. Elissen-Roman, J.-W. Weener, M. W. P. L. Baars, S. J. van der Gaast, E. W. Meijer, *J. Am. Chem. Soc.* **1998**, *120*, 8199 – 8208, and references therein.

[68] For non-dendronized polymers with a similar polarity pattern, see H. M. Janssen, E. Peeters, M. F. van Zundert, M. H. P. van Genderen, E. W. Meijer, *Macromolecules* **1997**, *30*, 8113 – 8128; T. Bjornholm, D. R. Greve, N. Reitzel, T. Hassenkam, K. Kjaer, P. B. Howes, N. B. Larsen, J. Bogelund, M. Jayaraman, P. C. Ewbank, R. D. McCullough, *J. Am. Chem. Soc.* **1998**, *120*, 7643 – 7644.

[69] For a discussion on the impact of the hydrophilicity/hydrophobicity ratio on the aggregation behavior of amphiphiles, see ref. [17].

[70] Y. Sayed-Sweet, D. M. Hedstrand, R. Spinder, D. A. Tomalia, *J. Mater. Chem.* **1997**, *7*, 1199 – 1204; O. Karthaus, K. Ijiro, M. Shimomura, *Langmuir* **1996**, *12*, 6714 – 6719; J. C. M. van Hest, D. A. P. Delnoye, M. W. P. L. Baars, C. Elissen-Roman, M. H. P. Genderen, *Chem. Eur. J.* **1996**, *2*, 1616 – 1626; F. Cardullo, F. Diederich, L. Echegoyen, T. Habicher, N. Jayaraman, R. M. Leblanc, J. F. Stoddart, S. Wang, *Langmuir* **1998**, *14*, 1955 – 1960; see also P. M. Saville, P. A. Reynolds, J. W. White, C. J. Hawker, J. M. J. Fréchet, K. L. Wooley, J. Penfold, J. R. P. Webster, *J. Phys. Chem.* **1995**, *99*, 8283; P. M. Saville, J. W. White, C. J. Hawker, K. L. Wooley, J. M. J. Fréchet, *J. Phys. Chem.* **1995**, *99*, 8283; Z. Bo, X. Zhang, X. Yi, M. Yang, J. Shen, Y. Rehn, S. Xi, *Polym. Bull.* **1997**, *38*, 257 – 264.

[71] J. P. Kampf, C. W. Frank, E. E. Malmström, C. J. Hawker, *Langmuir* **1999**, *15*, 227 – 233.