2. Synthesis of unpolar dendronized polystyrene

2.1. Some general comments

As has been described above, the first task of this project was to synthesize dendronized polymers with higher generations (3 and above), higher molecular weight and functional groups at the periphery.

A poly(*para*-phenylene) with fourth generation (G4) dendrons was synthesized using Suzuki polycondesation (SPC).[22] Unfortunately, it has no functional groups on its periphery, which rendered surface modification impossible. Besides this, computer generated space-filling models reveal that this polymer is unlikely to be highly rigid in spite of its very spatially demanding substituents. Although these dendrons are the largest ones ever attached to a polymer, and the backbone is commonly considered as a rigid-rod, there is still considerable space between consecutive dendrons this will allow the backbone to bend. Responsible for this space is the relatively large distance of approximately 8.5 Å between the dendron anchor sites along the backbone. From a computer model of a polystyrene with G3 dendrons, a much more compact structure is obtained although the dendrons are less demanding.[22] Besides some possible backbone contraction, the respective distance of only 2.5 Å seems to be responsible for this, although these factors cannot yet be differentiated. This computer model suggests how to proceed on the way to more rigid structures. A vinyl polymer, which has the 2.5 Å repeat unit, should be prepared with G4 dendrons on every repeat unit.

According to the previous results on the polymerisation of dendronized vinyl monomers,[21] there is a decreasing trend of the molecular weight with an increasing size of the attached dendrons. This trend was expected to render difficult the achievement of the above targets by the macromonomer route. In contrast to this, the attach-to route becames attractive for the preparation of higher molecular weight vinyl polymers having higher generation dendrons.

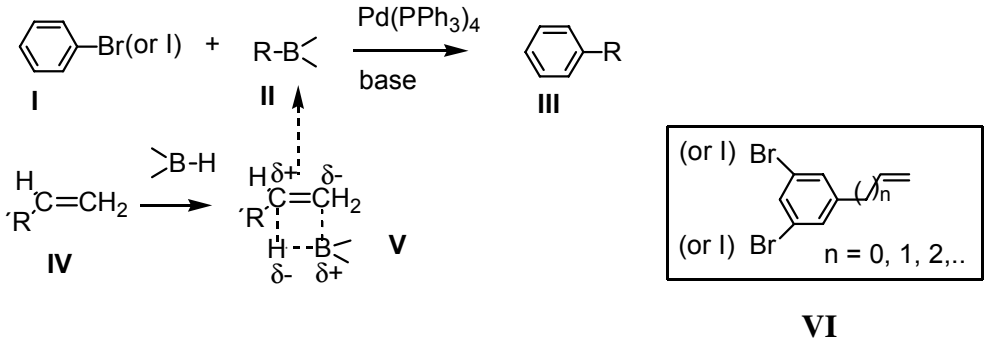
The main hurdle associated with the attach-to route is the difficulty of characterisation of the resulting polymers. In order to make the characterisation easier, first, it was tried to synthesize some structurally simple model polymers to investigate the feasibility of

the preparation of polymers bearing higher generation dendrons by attach-to route. This is specifically so in regarding to the question of which degree of coverage was achieved. This question can in principle be investigated with high field NMR spectroscopy. This requires, however, that functional groups of the starting polymer which have reacted with dendrons can be differentiated from those which have not. In order to experimentally prove the feasibility of NMR spectroscopy as an analytical tool for that purpose, some model studies for the attach-to route were performed.

To keep the models as easy as possible, they were designed to have as little as necessary functional groups.

It was intended to prepare some dendronized monomers, which only consist of methylene and phenylene moieties (unpolar), and to investigate the possibility of polymerisations.

In most cases, sp^2 carbon are connected to one another. There is however, also a report according to which an sp^2-carbon should be connected to an sp^3 one. This reaction requires an aryl halide and a 9-BBN derivative which at boron carries the sp^3-C-substituent to be connected. Suzuki coupling reaction is an ideal reaction for the



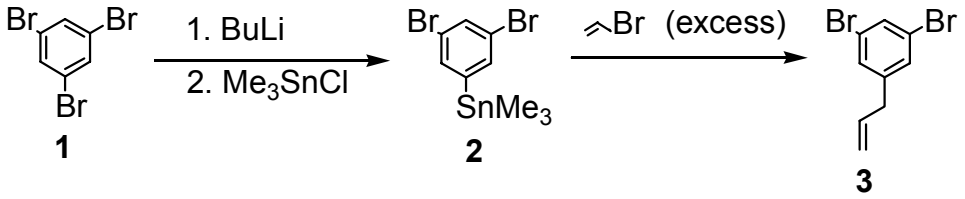
Scheme 4. Principle of cross-coupling of aryl/alkyl, compound **VI** is a representative one for this cross-coupling reaction.

formation of carbon-carbon bond.[23-26] The synthetic route to compound III is shown in Scheme 4. In the presence of base and Pd-catalyst, alkylation of aryl halides with organoborane such as trialkylborane and B-alkyl-9-borabicyclo [3.3.1]nonane (B-R-9-BBN) obtained by the reaction of 9-BBN and corresponding olefin can occur readily.

For the synthesis of dendrons, it is necessary to use an AB_x building block. A general structure (VI) is shown (Scheme 4), which carries halide and allylic functional groups. In this thesis, allylic dibromobenzene was prepared and used in the synthesis of unpolar dendrons. The detailed synthetic sequence will be discussed in the following part.

2.2. Synthesis of unpolar G1 and G2 dendrons

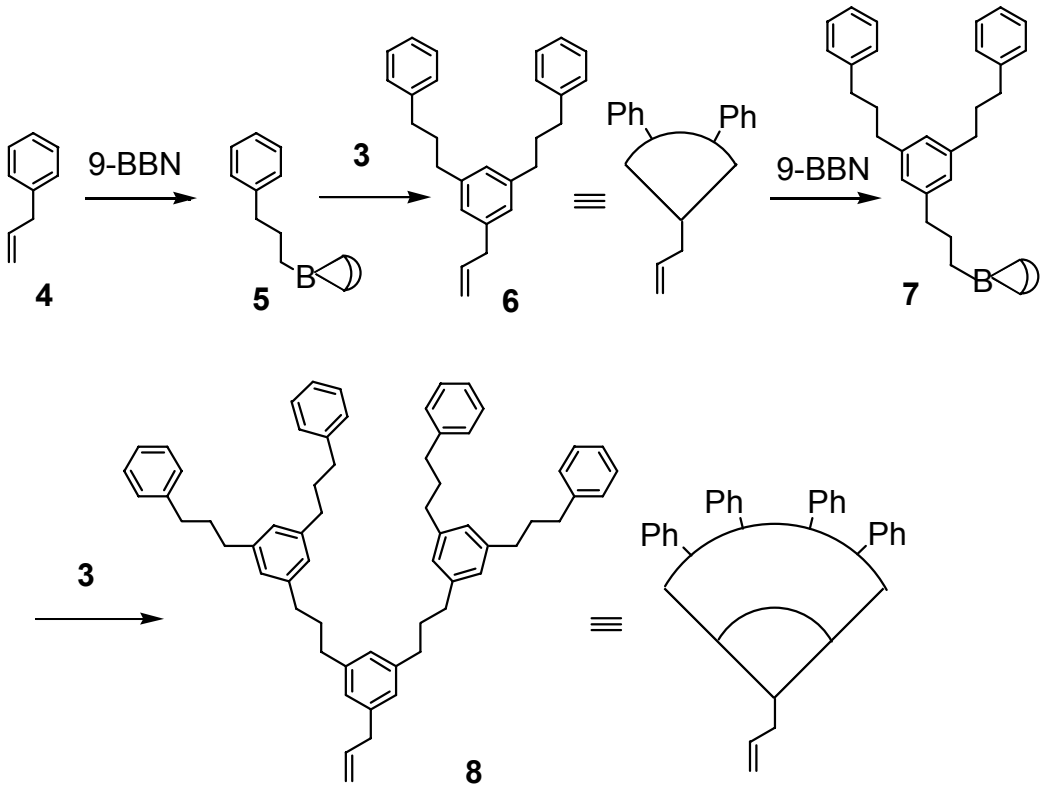
According to the above construction principle (Scheme 4), it was tried to synthesize allylic dibromobenzene as the unpolar dendritic building block. Scheme 5 depicts the synthetic sequence to compound **3**. Compound **2** was prepared according to literature procedure[27] using tribromobenzene as starting material. Compound **2** has the tendency to react in virture of a Stille reaction between its two kinds of functional groups under Suzuki reaction conditions.[27,28] In order to lower this side reaction, allylic bromide was used in large excess (2-3 equiv.). Reaction of **2** with allyl bromine in the presence of 1 mol% $Pd(PPh_3)_4$ as catalyst afforded compound **3** on the 25 g scale after column separation and destillation.



Scheme 5. Synthesis of compound **3.**

The synthetic sequence to compound **8**, a second generation completely unpolar dendron, is presented in Scheme 6. Starting material **4** was first converted to borane **5** by hydroboration. Compound **5** was used without separation for the next step. The yield of **5** from **4** was beyond 96% according to ^1H NMR spectrum measurement. Cross-coupling of **5** with **3** in the presence of 1 mol% $Pd(PPh_3)_4$ as catalyst precursor afforded

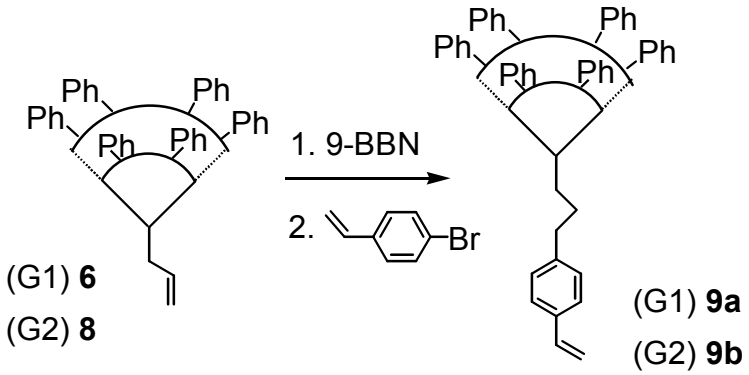
the branched compound **6**, which carries one olefin functional group at the focal point. Repetition of the hydroboration of **6** and cross-coupling with **3** gave compound **8** in 48 % yield after chromatographic separation.



Scheme 6. Synthesis of unpolar G1(**6**) and G2 (**8**) dendrons using Suzuki cross-coupling.

2.3. Synthesis of G1 and G2 monomers

The synthesis of G1 and G2 monomers (Scheme 7) based on dendrons **6** and **8** was performed by using the same sequence of hydroboration and cross-coupling with p-bromostyrene. The monomer structures were confirmed by the correct data of the elemental analysis, mass spectrometer and ^{1}H and ^{13}C NMR spectroscopy. The resulting monomers **9a** and **9b** are viscous oil.



Scheme 7. Synthese of G1 and G2 monomers **9a** and **9b**.

2.4. Polymerisation of unpolar monomers

2.4.1. Brief introduction of the polymerization of macromonomers

Dendronized polymers are a subclass of comb polymers. Some comprehensive reviews [29, 30] are available concerning polymerizations of dendritic monomers and related properties of the resulting dendronized polymers.

The synthesis of dendronized polymers from macromonomers has been developed broadly in recent years. The polymerisation procedure used can be devised into a) radically initiated chain growth and b) step-growth polymerisation (polycondensations). For example, styrene and acrylate carrying dendrons of first and second generation dendrons and poly(para-phenylene) with G4 dendrons have been prepared by (a) and (b), respectively.

Since dendronized polymers are a subclass of comb polymers, their polymerisation behaviour was expected to be similar.

For comb-like polymers, the kinetic apparently follows the conventional square-root equation for the overall rate of polymerisation, R_p: $R_p=k_p(2K_df/K_t)^{1/2}[I]^{1/2}[M]$ (1), where k_p and K_t are the rate constants of propagation and termination, respectively. K_d and f are rate constants of initiator decomposition and initiation efficiency, respectively. [I] and [M] are the concentrations of initiator and monomer, respectively. Therefore, we also have the conventional expression for the kinetic chain length (defined as the mean number of molecules of monomer that polymerise as the result of a single act of initiation), γ: $\gamma = K_p[M]/\{(2K_dfK_t)^{1/2}[I]^{1/2}\} = (1+X)DP_n^{\circ}/2$ (2)

where DP_n° is an instantaneous number-average degree of polymerisation assuming no chain transfer and X is the fraction of disproportionation in the termination step. Due to severe steric restriction of two multibranched radicals, the K_t values are very low.

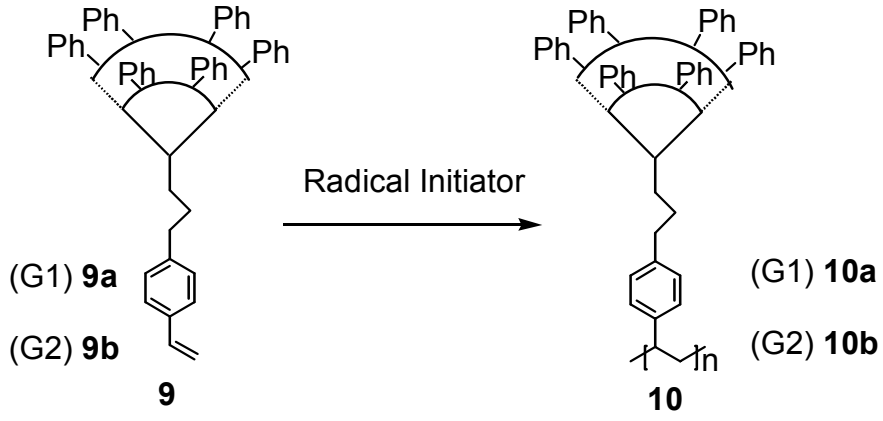
As a result, by virtue of Eqs. (1) and (2), the macromonomers may polymerize even more rapidly and to a higher degree of polymerisation than corresponding small monomers, supposed the polymerisation is carried out at the same concentration of [M] and [I]. Unfortunately, because the molar mass of the macromonomers is very high,

solution with high [M] is impractical. In general, the polymerisation of macromonomers leads to low molecular weight (MW) materials. Consequently, these polymers are nearly spherical and resemble star polymers in dilute solution. However, in recent years, in the particular case studied, polystyrene macromonomers[31] linked by an ethylene oxide spacer to an end-standing methacrylate group have been polymerized to DP=1000. and have a rodlike conformation in dilute solution. V. Percec et al. reported that G1 and G2 monomer with alkyl chains at the periphery have unusual polymerisation behaviour. It was found that self-assembly and self-organization with slow monomer diffusion produces an increased concentration (M) of polymerizable groups, a low f, and steric hindrance around the rigid and crowded growing chain generates a low k_t. this combination of effects yields high DP poly(monodendron)s in very high conversion and short reaction time (3 to 5 min) by using short half-life time initiators (AIBN at 90 °C, $t_{1/2}$ = 25 min).

For most of the dendronized polymers, the MW was obtained from GPC versus a polystyrene (PS) standard. The separation in a GPC experiment is based on the hydrodynamic volume (V_n) of macromolecules. Because of the large size of dendrons attached to the backbone, the hydrodynamic volume of dendronized polymers strongly deviates, however, from polystyrene. Consequently GPC results should be treated with care. Additionally, it was found that GPC normally underestimates molecular weights by a factor of 1.6-3.9.[30]

2.4.2. Polymerisation of G1 and G2 unpolar monomers 9a and 9b

Polymerisation (Scheme 8) was carried out in a 10 mL Schlenk tube sealed with a Rotaflo screw cap. The tube was charged with monomer and t-BPB initiator using toluene as solvent under nitrogen at 90 °C for 48 h. The crude polymer was dissolved in THF and precipitated in methanol/water. The resulting polymer was recovered and dried under high vacuum for 2 days. Attempts to lyophilised polymers **10** from benzene failed. They were always obtained as viscous oils. The results of polymerisation are summarised in Table 1. It can be seen that both G1 and G2 monomers **9b** can't yield high molar mass under the conditions applied. Weight percent was used, because the measurement of volume for the very small amount of monomers and solvent used was



Scheme 8. Polymerisation of G1 and G2 macromonomers **9a** and **9b**.

Table 1. Polymerisation of G1 and G2 Macromonomers and the Results

polymer	monomer conc. (wt.)	initiator	T (°C)	solvent	M_n ($\times 10^4$)	M_w/M_n	yield (%)	P_n
10a	34.7	BPB	90	toluene	0.97	4.3	40	21
10b	51.9	BPB	90	toluene	5.2	2.4	75	56

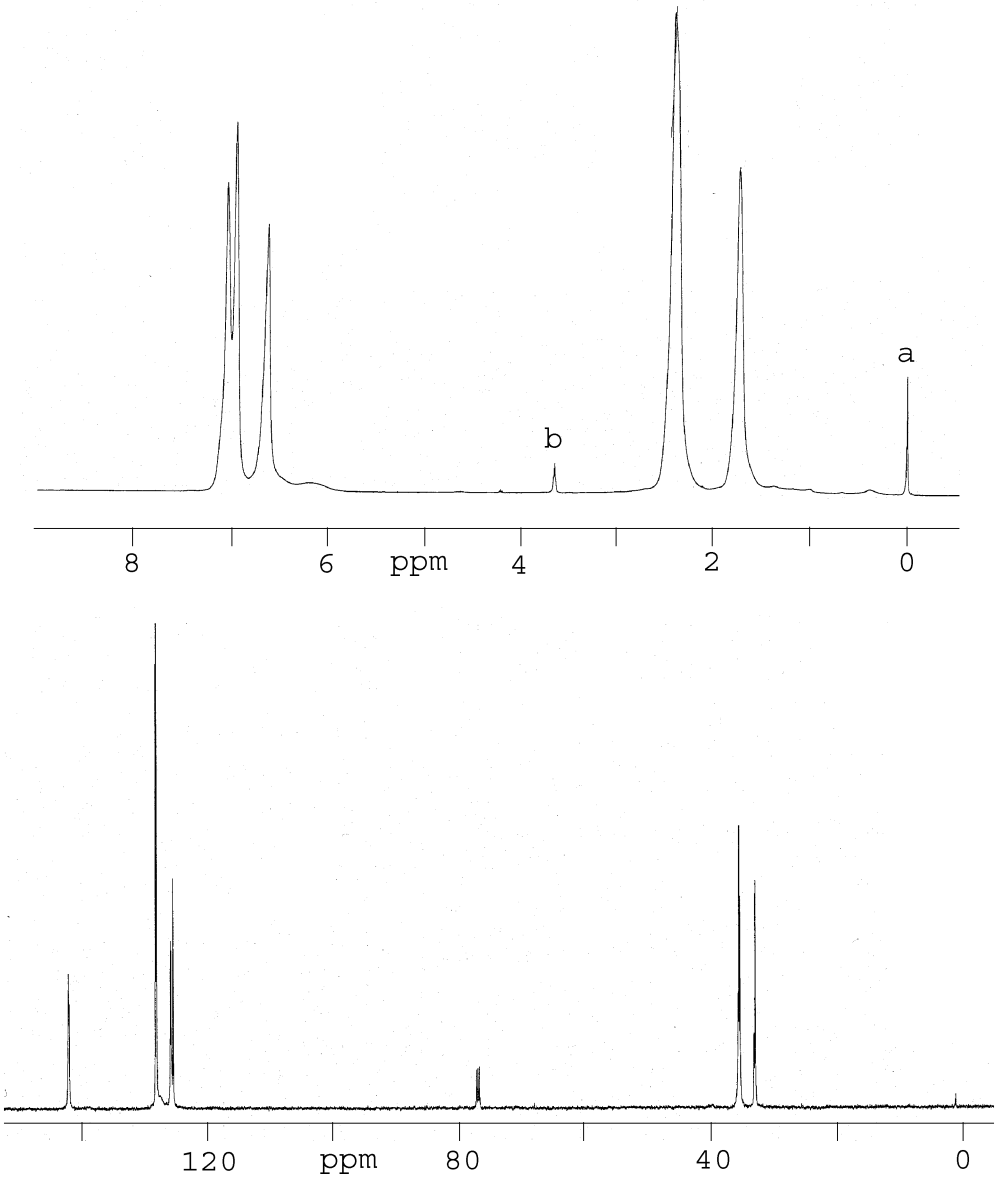


Fig. 5. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of polymer **10b**. Peak a indicates grease and peak b is solvent (THF).

difficult. It can be seen that G2 monomer is easier to yield higher molar mass and conversion. Figure 5 shows the proton and carbon NMR spectra of polymer **10b**. All the peaks appear as expected. From these simple spectra, it can be seen that these unpolar polymers are ideal candidates for the attach-to strategy if their surface bears functional groups (e.g. amine or hydroxyl groups).