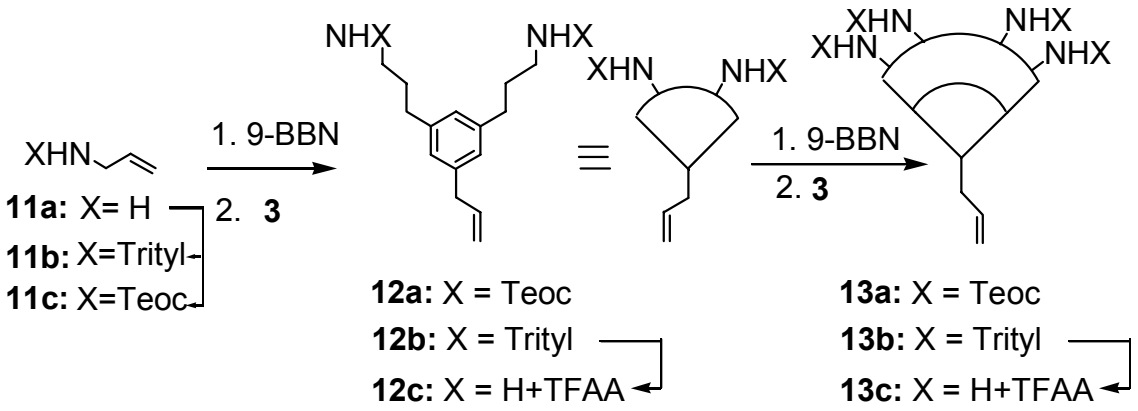
3. Synthesis of unpolar dendronized polystyrene with protected amine groups

The monomers synthesized above do not carry functional groups. This restricts their applications as model polymers for further modification and increase of generation by the attach-to route. The next logical step was therefore to introduce functional groups in the periphery of these attached unpolar dendrons.

Here, amines were selected because, considering their rich chemistry, they are ideal functional groups to bring about various chemical modifications of the targeted polymers including dendronization and biorelated ones. This matter also relates to one of our major goals in this research, which is to learn how to do surface engineering of dendritic nanocylinders.

3.1. Synthesis of G1 and G2 dendrons with protected amino functional groups

The preparation of G1 and G2 dendrons with protected amine groups is illustrated in Scheme 9. Trityl and Teoc were chosen as protecting groups for cost and solubility reasons, respectively. The more commonly used tert-butyloxycarbonyl (Boc) as protecting group for amines was also tried but found to be much inferior mostly for purification reasons. The precursor for trityl is commercially available at low cost, the solubility of tritylated compounds, however, is generally not very high. Since a high solubility of macromonomers can be critical in achieving high molar mass polymer, Teoc was also tried despite its relatively high cost and the additional synthetic effort associated with its use. The synthetic sequence to **13a** and **13b** involves protection of amine group and cross-coupling reaction. It was found that both Trityl and Teoc protected amino functional groups are inert to 9-BBN hydroboration of olefin. Reaction of compound **3** with adduct of 9-BBN and **11b** or **11c** in the presence of 1% of $Pd(PPh_3)_4$ afforded compounds **12a** and **12b** in yields of 79% and 81%, respectively. Repetition of the same procedures yields **13a** or **13b** in 70% and 61%, respectively.

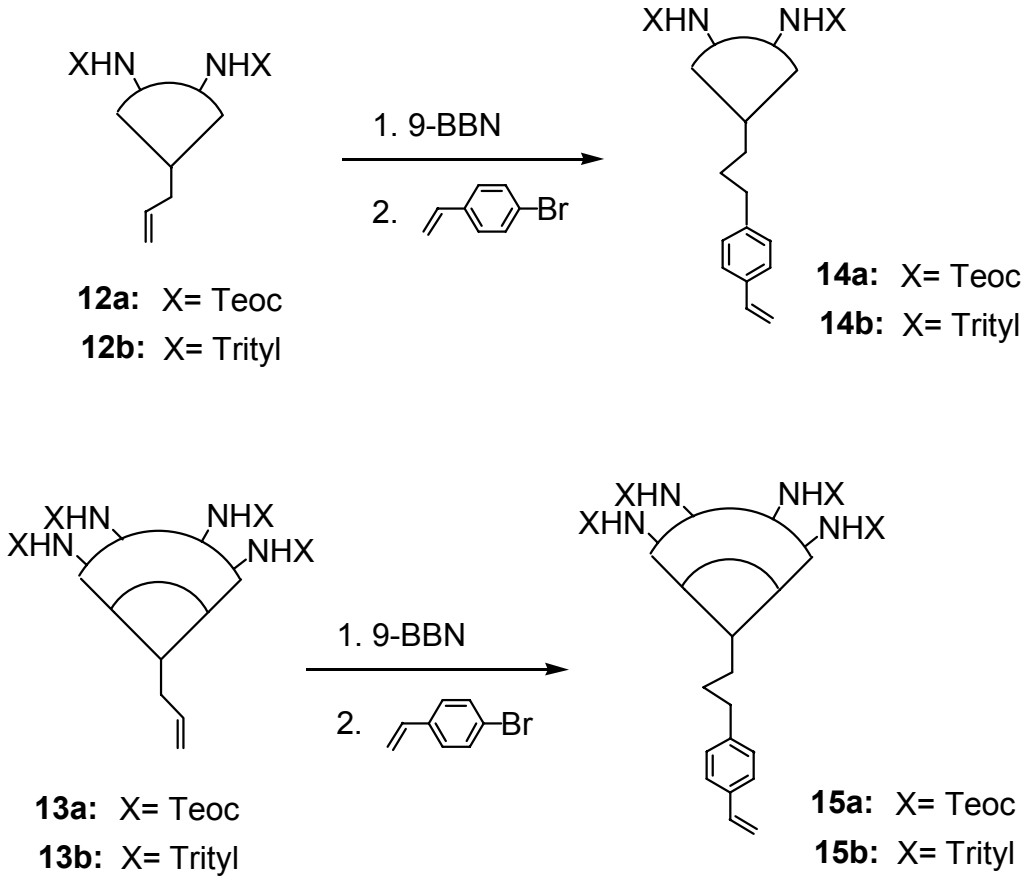


Scheme 9. Synthesis of G1 and G2 dendrons with amino protected groups.

These G1 and G2 dendrons can be deprotected to give the corresponding salts **12c** or **13c** by treatment with trifluoroacetic acid. Due to the cost consideration, it is reasonable to choose trityl protected compounds as candidates for deprotection. Deprotection of G1 and G2 dendrons **12b** and **13b** was carried out in methylene chloride using methanol as a scavenger for the Trityl group. It was found that trityl group is difficult to be totally removed by one time treatment. To drive this deprotection to completion, at least two deprotection steps were necessary. The course of the deprotection can be monitored by ^{1}H NMR and ^{13}C NMR spectra . The obtained deprotected G1 and G2 dendrons can be used as starting material for the synthesis of polarity gradient higher generation polymers.

3.2. Synthesis of G1 and G2 monomers with protected amino functional groups

The attachments of polymerisable groups to G1 and G2 dendrons were accomplished by applying the same hydroboration and cross-coupling reaction using p-bromostyrene as for **9a**.



Scheme 10. Synthesis of G1 (**14a, 14b**) and G2 (**15a, 15b**) macromonomers.

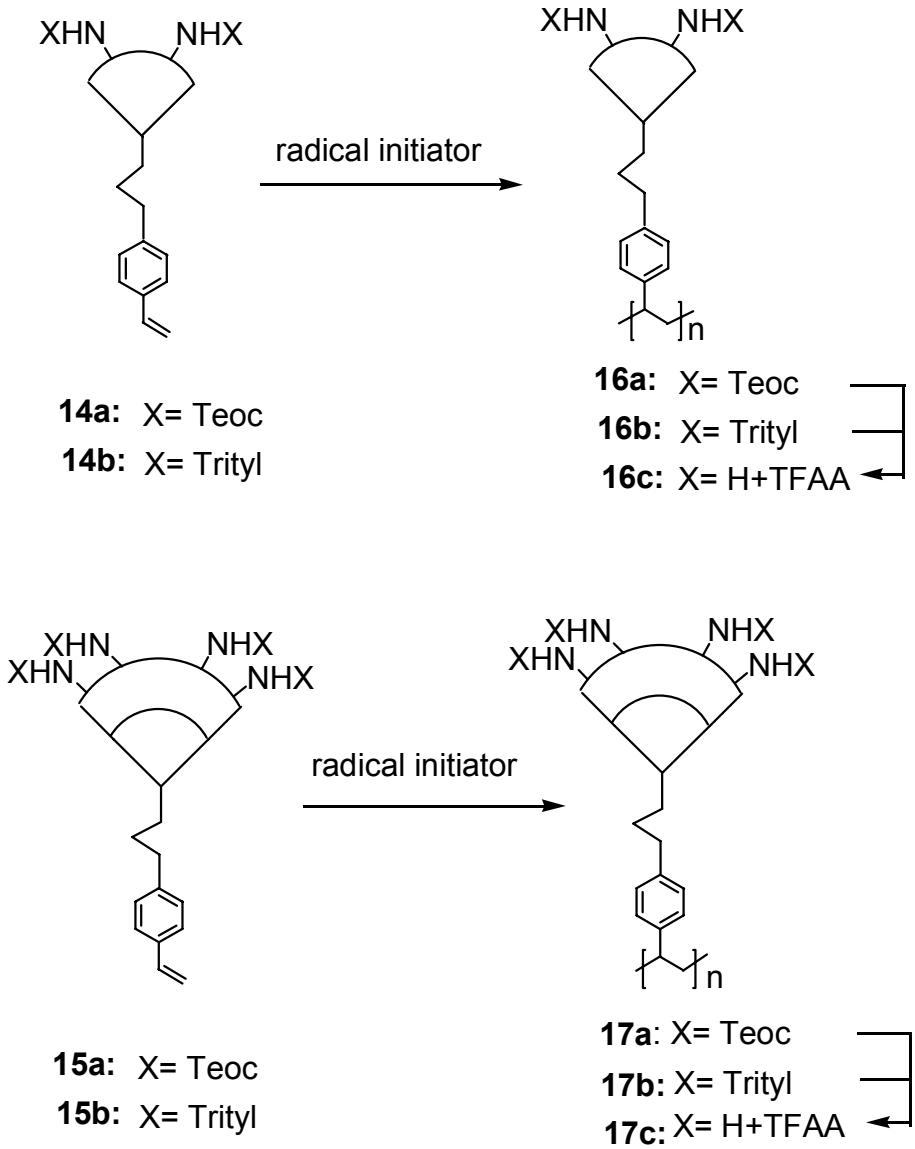
The synthetic steps are given in Scheme 10, in which G1 and G2 monomers bearing protected amine groups have been synthesized. The yields for G1 and G2 monomers were 67% (G1-Teoc), 69% (G1-Trityl), 45% (G2-Teoc) and 30% (G2-Trityl) after chromatographic separation (silica gel, hexane/ethyl acetate as eluent). It is clear that the

yields for the cross-coupling reaction decreased with the increase of generations. All the monomers were characterised by the ^{1}H and ^{13}C NMR spectra, mass spectrometer and correct data of element analysis. The signals of the Teoc groups appear at δ = -0.05, 0.90 and 4.10 ppm. The signals of the Trityl groups appear at δ = 7.10 and 7.38 ppm. The signals at δ = 5.18 (d), 5.70 (d) and 6.69 (dd) belong to the protons of double bond. All the other signals from ^{13}C NMR spectrum appear as expected and were fully assighned.

3.3. Polymerisation of G1 and G2 macromonomers

The polymerisations of G1 and G2 monomers **14** and **15** are outlined in Scheme 11. They were carried out according to similar procedures as described above. Table 2 displays the conditions and results of polymerisation of G1 macromonomer **14b**. It was found that no polymerisation takes place at temperature less than 70 °C with both AIBN and BPO as initiators. At higher temperature (for example 90 °C), some polymers were detected by GPC, however, the conversion was very low (less than 21%). Both low yield and molar mass was achieved at 80 °C. Several different monomer concentrations were tried, but there were no significant change in the polymerisation results. Changing the solvent from toluene to diethyl ketone improved the situation for polymer **16b** obtained from tritylated G1 monomer. but the molar masses did not increased much. The main problem encountered here is that the solubility of Trityl-protected monomers is not good, rendering polymerisation at higher concentration impossible. The similar situation have also been observed previously in other systems.[32]

Table 3 summarised the best conditions and results obtained. As can be seen, Teoc protected monomers **14a** and **15a** gave higher molecular weight than Trityl protected ones **14b** and **16b**. A reason for the superiority of Teoc over Trityl monomers may be the higher solubility of the former which allows one to apply higher concentrations. It should be noted here that the polymerization mixture of tritylated monomers in Table 2 and 3 were not homogeneous in toluene. The actual concentrations are therefore lower than the data given.



Scheme 11. Polymerizations of monomers **14a**, **14b**, **15a** and **16b**, together with their deprotections of the resulting polymers **16a**, **b** and **17a**, **b**, respectively.

Table 2. **Polymerisation of G1-Trityl Macromonomer 14b and the Results**

polymer	monomer conc. (mol/L)	initiator	T (°C)	solvent	M_n ($\times 10^4$)	M_w/M_n	yield (%)	P_n
16b	0.62	AIBN	50	toluene	--	--	--	--
16b	0.62	BPO	70	toluene	--	--	--	--
16b	0.62	BPO	80	toluene	0.92	1.1	13	11
16b	0.55	^{t}BPB	90	toluene	2.1	1.8	21	26
16b	0.62	^{t}BPB	90	toluene	2.4	2.2	15	29
16b	0.67	^{t}BPB	90	toluene	2.0	1.9	20	24

Table 3. **Polymerisations of G1 and G2 Macromonomers 16a**, **b**, **17a**, **b and the Results**

polymer	monomer conc. (mol/L)	initiator	T (°C)	solvent	M_n ($\times 10^4$)	M_w/M_n	yield (%)	P_n
16a	0.68	AIBN	55	toluene	3.8	2.44	85	60
16b	0.62	^{t}BPB	90	toluene	2.1	1.84	17	25
16b	0.62	^{t}BPB	90	dk*	2.6	2.78	79	32
17a	0.45	^{t}BPB	90	toluene	5.0	1.94	86	39
17b	0.45	^{t}BPB	90	dk*	2.0	1.76	28	14
17b	0.26	^{t}BPB	90	toluene	3.7	1.35	63	13

*dk: diethyl ketone

3.4. Deprotection of G1 and G2 dendronized polymers with protected amino functional group

Samples of all polymers (**16a**, **16b**; **17a** and **17b**) with the molar masses given in Table 3 were deprotected with trifluoroacetic acid in methanol solution (polymers **16b** and **17b**) or neat (polymers **16a** and **17a**). The acid was used in an excess of 1-2 equiv. per functional group. For the Teoc polymers **16a** and **17a**, a single acid treatment was sufficient. The completeness of deprotection was proven by the highly resolved ^{1}H NMR spectrum of the deprotected polymer which had an excellent signal-to-noise ratio. Figure 6 shows the ^{1}H NMR spectra of polymer **17a** and its deprotected corresponding

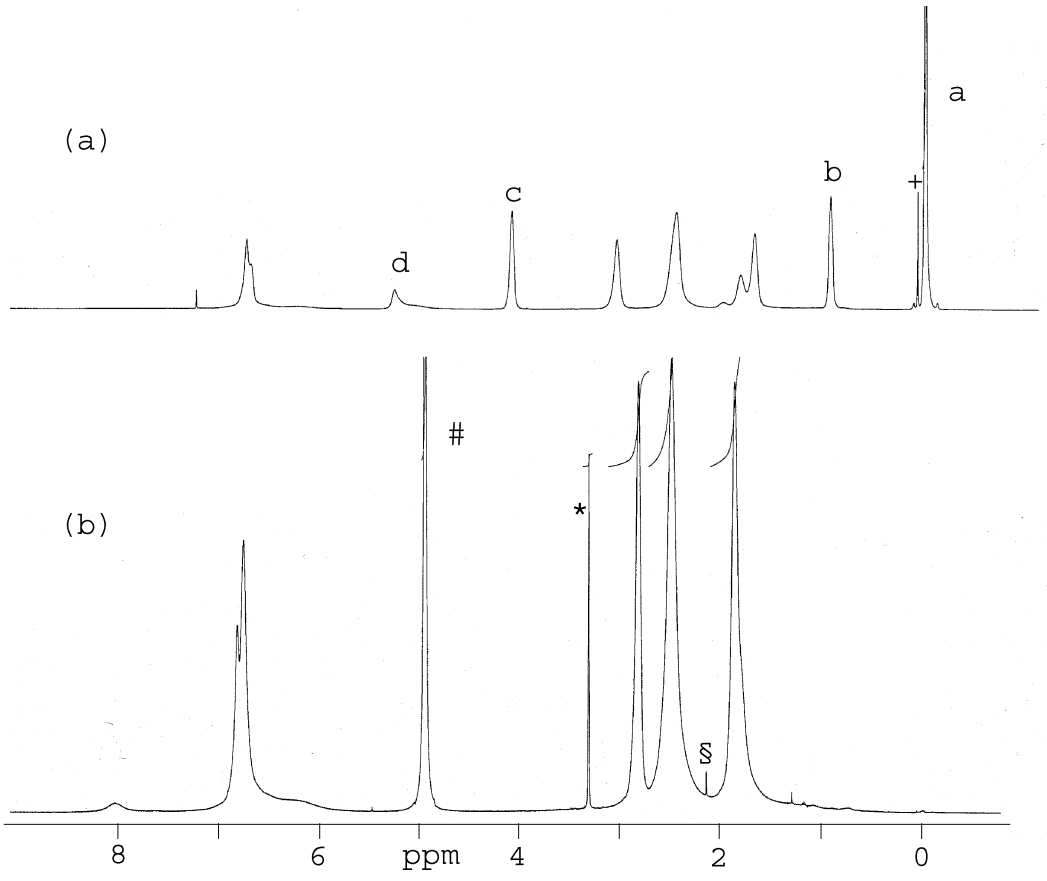


Fig. 6. ^{1}H NMR spectra of **17a** (a) and **17c** (b). [* CD_3OD; § remaining solvent; a, b, and c Teoc protecting group; d amide; # water; + grease]

polymer **17c.** The signals of the Teoc group at δ = -0.05, 0.90 and 4.10 ppm and that of the Trityl group at δ = 7.10 and 7.38 disappeared completely. Peak d in (b) belongs to the proton of the amide, which can not be seen in CD_3OD solvent. It is obvious that the deprotection is complete from the disappear of the peaks corresponding to Teoc protecting groups. It had to be repeated 2-3 times for the Trityl protected polymers. All of the deprotected polymers are water and methanol soluble, and represent novel polyelectrolyte. The major applications here are to use them as the raw polymers for surface modifications.