Electronic Supplementary Material (ESI) for Soft Matter.

NMR spectra assignment

Table 1 represents the chemical shifts for PMSSO dendrimers G1-G5. The first column specifies the generation of the dendrimer followed by the notation of the constituting unit. The character d corresponds to the range in which all d units appear for a given dendrimer.

Table 1. Chemical shifts in ^{1}H, ^{13}C and ^{29}Si for different units of PMSSO dendrimers G1-G5

Line	^{29}Si		^{13}C		^{1}H	
	Range	Maximum	Range	Maximum	Range	Maximum
G1; d0	(-67,2;-69,2)	-69,04	--	-2,378	(0,08;0,05)	0,09
G1; d1	(-65,7;-66,2)	-65,93	--	-2,1	(0,05;0,02)	0,04
G1; t2	(7,9;7,2)	7,57	--	1,736	(0,17;0,07)	0,1
G2; d	(-67,4;-66,2)	--	(-1,76;-3)	--	--	--
G2; d0	(-67,4;-68,6)	-68,41	--	--	(0,18;0,17)	0,18
G2; d1	(-68,6; -68,9)	-68,771	--	-2	(0,14; 0,13)	0,14
G2; d2	(-64,8;-66,2)	-66,024	--	-1,86	(0,06;0,04)	0,06
G2; t3	(8,6;7,1)	7,31	--	1,79	(0,12;0,08)	0,1
G3; d	(-64,2;-69,9)	--	(-1,7;-3,24)	-2,07	--	--
G3; dN	(-64,2;-66,3)	-65,88	--	--	(0,06; 0,01)	0,04
G3; d(N-1)	(-66,3;-67,7)	-67,21	--	--	--	--
G3; dR	(-67,7;-69,9)	-68,72	--	--	(0,26;0,1)	0,15
G3; t4	(10; 6,3)	7,47	(1,89;1,39)	1,73	(0,1;0,07)	0,09
G4; d	(-64;-70)	--	(-1,44;-3,38)	-2,03	--	--
G4; dN	(-64;-66,3)	-65,95	--	--	(0,07;0,01)	0,04
G4; d(N-1)	(-66,3; -67,6)	-67,26	--	--	--	--
G4; dR	(-67,6;-70)	-68,72	--	--	(0,26;0,1)	0,15
G4; t5	(10; 6,7)	7,33	(2,14;1,37)	1,75	(0,1;0,07)	0,09
G5; d	(-64;-70,5)	--	(-1,57;-3,22)	-1,95	--	--
G5; dN	(-64;-66,3)	-65,98	--	--	(0,07; 0,01)	0,04
G5; d(N-1)	(-66,3;-67,85)	-67,13	--	--	--	--
G5; dR	(-67,85;-70,5)	-68,76	--	--	(0,26;0,1)	0,15
G5; t6	(10;6,4)	7,31	(2,28;1,23)	1,76	(0,11;0,07)	0,09

In addition to the most intensive signals due to the perfect dendrimer molecules, for some samples the signals corresponding to dendrimers with defects were found. Particularly, in the ^{29}Si spectra of dendrimer G1 a series of the lines with intensities 1:2:4 was found. These signals were assigned to the first generation PMSSO dendrimer molecule in which the single terminal $(d1)_1(t2)_2$ unit is absent. The chemical shifts for these compounds reveal the common trend with the main molecule: -65.71 (d0'); -65.88(d1'); 7.60 (t2'). For dendrimer G2 two dendrimer molecules were identified in which two terminal blocking units are absent. Similarly to the G1 dendrimer the most prominent differences of chemical shift were observed for d0 units. These differences decrease with the decrease of the distance from the core of dendrimer. For lines d2 and t3 of dendrimer G2 the signals of "defects" cannot be distinguished from the signals of the main compound ("perfect" dendrimer molecule). The possible defects in the structures can be generally attributed to the deficiency of the terminal units and to a lesser extent to the missing arms. This implies that the defects are mainly formed on the blocking stage of the synthesis. The general tendency typical for the "perfect" structures can be seen: the ratio of the intensities t/dN/d(N-1) approximately correspond to 1/0.5/0.25 (Table 2 in the text of the article). The spectral lines which can be ascribed to intramolecular loops were not observed. The relative integral intensities of the lines in ^{29}Si confirm the low content of "imperfect" dendrimers.

Figures 1 and 2 illustrate the data of the table 1 for chemical shifts in the 1H and 29Si spectra of PMSSO dendrimers, respectively. The lines indicate the trends of changes of the chemical shifts with increasing generation number for specific structural units. The order of the lines in ^{1}H spectra in contrast to ^{13}C and ^{29}Si is not strictly ascending/descending. The lines follow the order dN, t(N+1), d(N-1), dR in order of increasing chemical shift (Fig. 1). This shows that the influence of t units on the chemical shift extends for the two neighboring cascades of dendrimers similarly to the case of ^{29}Si spectra. The chemical shift of t region has tendency of slight upfield shift of maximum with increasing generation number. For dendrimers of the third and higher generations lines d(N-1) and dR in 1H spectra are not resolved and appear as a downfield shoulder of the t(N+1) line. The intensity of the shoulder is higher near the t(N+1). This shows that the d(N-1) occupy a smaller range of chemical shifts compared to dR units. The maxima of dR and d(N-1) units were assigned nominally in table 1 and Fig. 1 for dendrimers G3-G5 to specify the features mentioned above.

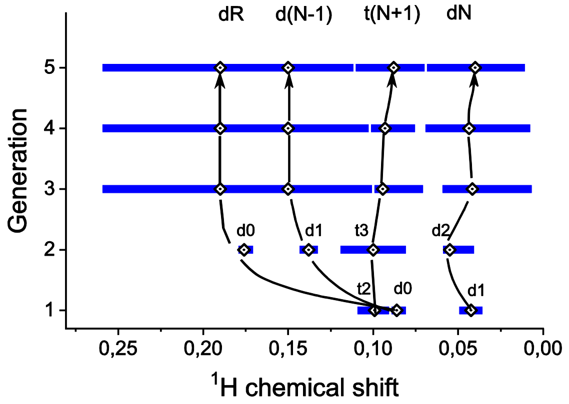

Figure 1. ^{1}H NMR chemical shifts for PMSSO dendrimers G1-G5

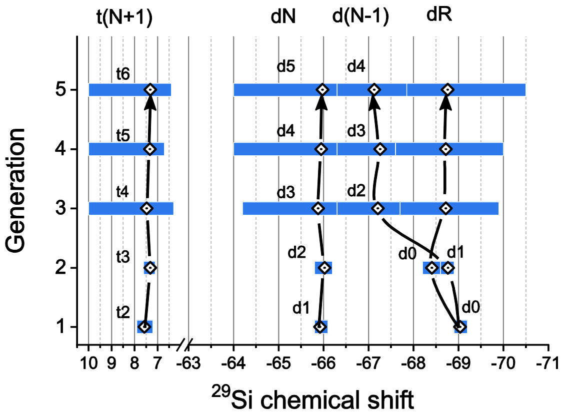

Figure 2. ^{29}Si NMR chemical shifts for PMSSO dendrimers G1-G5