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Many-Arm Star Polymers Synthesized Using Chlorosilane Linking Agents: Their Structural Quality Concerning Arm Number and Polydispersity

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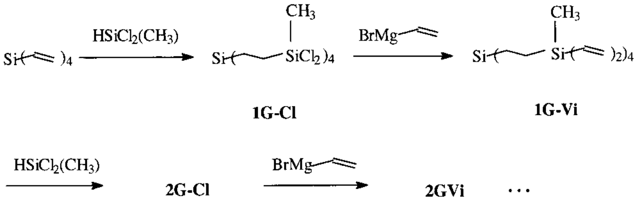
ABSTRACT: A series of polybutadiene star polymers were produced by coupling living poly(butadienyl)-lithium with dendritic chlorosilane linking agents. The theoretical arm numbers of the stars covered the range from 4 to 64, and the arm molecular weight was kept short with $M_{n(arm)} = 10^3$. MALDI-TOF MS and ^{1}H NMR spectroscopy were used to characterize the dendritic linking agents. The low $M_{n(arm)}$ also allowed the investigation of the star polymers by MALDI-TOF MS in addition to the classical characterization techniques. It was found that up to the star with 16 arms the structural quality with respect to functionality and polydispersity coincides with the theoretical values. In the case of the star polymers with theoretically 32 and 64 arms, the average functionalities found for the chlorosilane dendrimers were 31 and 60, respectively, and the polydispersities were considerably smaller than 1.01. The corresponding star polymers had average arm numbers of approximately 29 and 54, along with molecular weight distributions of 1.01 and 1.02, respectively.

Introduction

Star polymers play an important role in polymer physics. Their dilute and semidilute solution properties have been studied extensively.[1−5] For these studies and the comparison with theoretical models, it is essential to use well-defined materials. The coupling of polymer chains containing a living anionic end group with multifunctional chlorosilane dendrimers is the method of choice for the production of well-defined star polymers with low polydispersities. Using this method, star polymers with arm numbers or functionalities ($f_{(star)}$) of up to 128 have been synthesized.[6]

In the past, size exclusion chromatography (SEC), light scattering, and osmometry measurements have been used to characterize star polymers. For $f_{(star)} = 3$ and 4, high-resolution SEC is a good tool to check the extent of conversion of the arms into the star structure.[7−9] However, detailed analysis of star polymers with $f_{(star)} > 4$ is more difficult. The linking agents used for highly functional stars are dendritic chlorosilanes. If the conversions for the different steps during the dendrimer synthesis are incomplete, the effective functionality of the linking agent is lower than the theoretical one. Thus, a distribution of different functionalities is expected. The same effects result from incomplete coupling of the linking agent with the living chain ends. SEC analysis gives little information about the polydispersity of the product as the hydrodynamic volume changes very little with increasing arm number of the star polymer. For this reason the SEC trace of a many-arm star polymer having in reality a high polydispersity will be of perfect shape and simulates a narrow molecular weight distribution (M_w/M_n). The distributions extracted from combined light scattering and osmometry measurements are also of little help. The relative experimental errors of both methods are at least 5%, which means that distributions cannot be calculated with the precision needed.

Scheme 1. Preparation of the Chlorosilane Dendrimers



Therefore, we decided to use matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) for the analysis of the star polymers. This technique is ideal for our purpose as it enables the measurement of real molecular weights and not hydrodynamic volumes as SEC does. In the past, the characterization of dendrimers was successfully achieved using this technique.[10−16] On the other hand, the mass range accessible by MALDI-TOF MS is limited to lower masses. Therefore, polybutadiene (PB) star polymers with theoretical functionalities $f_{(theo)}$ of 4, 16, 32, and 64 and arm molecular weights of $M_{n(arm)} = 10^3$ were chosen for the analysis. Additionally, MALDI-TOF MS was used for the quality check of the dendritic linking materials.

Experimental Section

Synthesis of Stars. The dendritic chlorosilane coupling agents **1G-Cl**, **2G-Cl**, **3G-Cl**, and **4G-Cl** were synthesized according to a procedure described by Zhou and Roovers[17] (Scheme 1).

The polymerization and linking reactions were performed under high vacuum in glass reactors according to a procedure described by Roovers et al.[6]

Characterization. SEC experiments of the polymer arms and the star polymers were carried out at 30 °C, using a Waters 150C instrument and four μ-Styragel columns with a porosity range from 10^5 to 500 Å. The M_n values of the star

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polymers were measured with a Knauer membrane osmometer using toluene as solvent. ^1H NMR spectroscopy (500 MHz Bruker spectrometer) was used for the determination of $M_{n(arm)}$ by comparing the resonances of the *tert*-butyl initiator group at 0.9 ppm with the olefinic PB protons at 4.9 and 5.4 ppm.

The MALDI-TOF MS measurements of the star polymers and the dendrimers **1G-Vi**, **2G-Vi**, and **3G-Vi** were carried out with a Reflex I mass spectrometer (Bruker, Bremen, Germany), equipped with a 337 nm nitrogen laser. The spectra were recorded in the linear mode with the Bruker HIMAS detector at an acceleration voltage of 30 kV. The mass spectrometer was calibrated external with polystyrene (PS) (PSS, Mainz, Germany) before each measurement. The matrix 1,8,9-trihydroxyanthracene (dithranol) (Aldrich) and the samples were dissolved in THF and mixed at a mole ratio of approximately 1:500 (analyte:matrix). Silver or lithium trifluoroacetate, also dissolved in THF, was used for ionization via cation attachment. The MALDI-TOF MS spectra shown in this paper are smoothed and baseline corrected with the XMASS data processing program (Bruker).

Results and Discussion

The polydispersity of star polymers is determined by three factors: the polydispersity of the coupling agent with respect to functionality, the polydispersity of the polymer arm, and the completeness of the linking reaction of the living polymer chains with the coupling agent.

Using the chlorosilane linking routine, three- and four-arm star polymers are synthesized with the coupling agents methyltrichlorosilane and tetrachlorosilane which are commercially available in high purity. The linking reaction with living chain ends occurs without detectable amounts of side reactions, and conversion is complete for PB.[18,19] PS and polyisoprene (PI) chain ends are less reactive according to their bulkiness. In these cases complete conversion is achievable by capping the chain ends with a few units of butadiene.[20]

The synthesis of many-arm star polymers via the chlorosilane method affords the use of dendritic linking agents. The starting point for the synthesis of the dendrimers that we used is described in detail by Zhou and Roovers[17] (Scheme 1). In the first step tetravinylsilane was hydrosilylated with dichloromethylsilane ($HSiCl_2(CH_3)$) to yield the eight-functional linking agent **1G-Cl**. In the next step the chlorine atoms in **1G-Cl** were replaced by vinyl groups, using vinylmagnesium bromide. This molecule is denoted **1G-Vi**. The continuation of the procedure yielded the linking agents **2G-Cl**, **3G-Cl**, and **4G-Cl** for the production of the 16-, 32-, and 64-arm stars, respectively. Samples of the linking agents in dry deuterated benzene were investigated carefully by ^1H NMR spectroscopy to check the completeness of the hydrosilylation reaction. In the cases of **1G-Cl** and **2G-Cl** no detectable signals for the vinyl group between 5.7 and 6.2 ppm were found. For **3G-Cl** and **4G-Cl** small remaining vinyl signals were correlated with 0.1% and 0.3% of unreacted vinyl groups in the dendrimer. The NMR analysis of the reagent $HSiCl_2(CH_3)$ revealed that the most likely and disturbing impurities $HSiCl_3$, $HSiCl(CH_3)_2$, and $HSi(CH_3)_3$, were present in less than 1% quantity.

Due to the moisture sensitivity of the Si−Cl groups in the chlorosilane dendrimers, MALDI-TOF MS measurements of the linking agents were not performed. The intermediate vinyl dendrimers **1G-Vi**, **2G-Vi**, and **3G-Vi**, however, were examined using this technique. The MALDI-TOF MS spectra of the vinyl dendrimers are shown in Figure 1. In the spectrum of **1G-Vi** (Figure 1a) no byproduct is visible within experimental error. The main signal in the **2G-Vi** (Figure 1b) spectrum with m/z = 1320.6−7.0 for Li (see Experimental Section) corresponds to the 16-functional vinyl dendrimer with the formula $C_{68}H_{132}Si_{13}$ and the calculated mass of

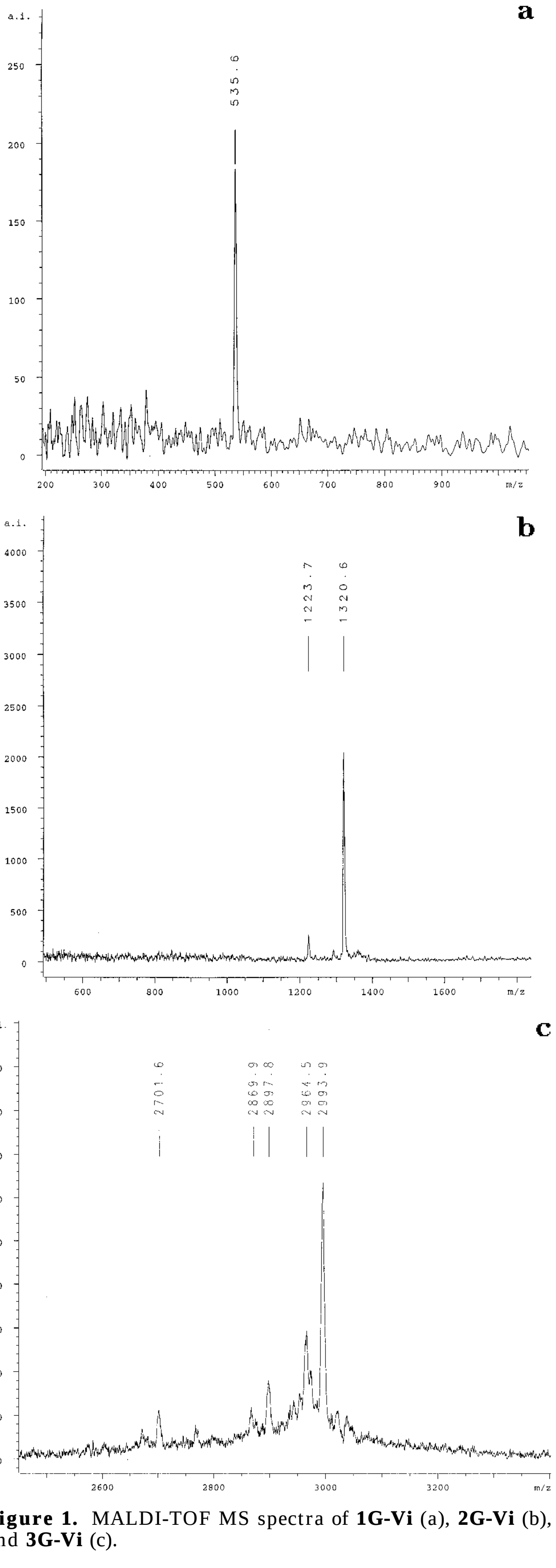

Figure 1. MALDI-TOF MS spectra of **1G-Vi** (a), **2G-Vi** (b), and **3G-Vi** (c).

1314.9. The mass of the second signal of $m/z = 1223.7-7.0$ is in good accordance with a structure having 14 vinyl groups. The loss of functionality in the latter case is due to the contamination of vinyl bromide with ethyl bromide. This impurity causes already during the formation of **1G-Vi** a fraction of dendrimer molecules having seven vinyl and one ethyl end group. In the MALDI-TOF MS spectrum of **1G-Vi** the defect structure is not visible. In that case the mass difference between the product and the side product is only two. Due to the low resolution of the employed detector, the signal of the side product is not visible. In **2G-Vi**, however, the dendrimer deriving from the **1G-Vi** defect structure and the formula $C_{63}H_{124}Si_{12}$ (calculated mass 1218.7) is detectable due to the higher mass difference and the better signal-to-noise ratio of the measurement.

Incomplete hydrosilylation of **1G-Vi** is not the source for the defect structure in **2G-Vi** as the NMR spectrum of **2G-Cl** shows no trace of remaining vinyl groups. The integration of the signal intensities yielded that **2G-Vi** contains 91% of the 16-functional dendrimer and 9% of the 14-functional dendrimer. These values are in good accordance with theoretical calculations assuming a mixture of 99% vinyl bromide and 1% ethyl bromide in the reagent as well as a binomial distribution of vinyl and ethyl groups in the dendrimer molecules. In that case **1G-Vi** should contain about 92% of dendrimer molecules consisting of eight vinyl end groups and 8% of structures having seven vinyl and one ethyl end group. Structures with more than one ethyl group per dendrimer molecule are present in nonsignificant quantities.

Knowing this, we can assume that in **2G-Vi** there are also about 1% of ethyl end groups, which are first detectable in the spectrum **3G-Vi** (Figure 1c) because of the increased mass difference. Indeed, besides the main signal in the **3G-Vi** spectrum with $m/z = 2993.9-107.9$ (for Ag), which corresponds to the 32-functional product $C_{148}H_{292}Si_{29}$ (calculated mass 2886.4), further signals appear. The signal at $m/z = 2897.8-107.9$ corresponds to the 30-functional side product with the formula $C_{143}H_{284}Si_{28}$ and the theoretical mass 2790.2. This structure derives from the replacement of one vinyl group in **2G-Vi** by an ethyl group. The signal at $m/z = 2701.6-107.9$ results from the 14-functional side product in **2G-Vi** and therefore has a functionality of 28, the formula $C_{133}H_{264}Si_{26}$, and a theoretical mass of 2593.8. The ratios of the signal intensities are again in good agreement with 1% of ethyl bromide impurity in the vinyl bromide being responsible for the structures with lower functionality. Due to the NMR analysis of the chlorosilane intermediates, we can exclude incomplete hydrosilylation being the main reason for the dendrimers of lower functionality. In contrast, Lorenz et al. found in a different study of carbosilane dendrimers using MALDI-TOF MS that incomplete hydrosilylation was the reason for defect structures.[16]

All three signals of **3G-Vi** discussed above show on the low molecular weight side additional small signals with the same difference in mass. These signals can be assigned to molecules where one or two vinyl groups are replaced by methyl groups in **3G-Vi**. The methyl groups originate from $HSiCl(CH_3)_2$ and/or $HSi(CH_3)_3$ impurities in $HSiCl_2(CH_3)$. From the intensity ratios of the MALDI-TOF MS signals, we estimated that 1% of excess CH_3 was present in $HSiCl_2(CH_3)$. The fact that comparable defects were not found in **2G-Vi** most likely is caused by the use of another batch of $HSiCl_2(CH_3)$ of higher purity in the latter case.

Table 1. Characterization of the Chlorosilane Dendrimers and the Intermediate Vinyl Dendrimers

dendrimer	formula	$M_{(calc)}$	$f_{(theo)}$	$f_{(dendrimer)}$ MALDI/NMR	f_w/f_n
	$SiCl_4$	169.9	4		
1G-Vi	$C_{28}H_{52}Si_5$	529.1	8	7.92	1.001
2G-Cl	$C_{36}H_{84}Cl_{16}Si_{13}$	1449.4	16	15.7	
2G-Vi	$C_{68}H_{132}Si_{13}$	1314.9	16	15.6	1.002
3G-Cl	$C_{84}H_{196}Cl_{32}Si_{29}$	3155.5	32	31	
3G-Vi	$C_{148}H_{292}Si_{29}$	2886.4	32	31	1.003
4G-Cl	$C_{180}H_{420}Cl_{64}Si_{61}$	6567.5	64	60	

Summarizing the results of the MALDI-TOF MS and NMR measurements, we conclude that impurities in the vinyl bromide and $HSiCl_2(CH_3)$, which cause unreactive end groups, are mainly responsible for defect structures. The contribution to the loss in functionality of incomplete hydrosilylation and incomplete substitution of the chlorosilane groups by the Grignard compound is negligible, at least up to the dendrimer **4G-Cl**.

Knowing the degrees of conversion and the purities of the reagents, we are now able to calculate the functionalities of the vinyl and the chlorosilane dendrimers ($f_{(dendrimer)}$). The values are listed in Table 1 together with the calculated values ($f_{(theo)}$). Additionally, the polydispersities of the vinyl dendrimers were extracted from the MALDI-TOF MS data. They are expressed in terms of f_w/f_n, where f_w denotes the weight-average f and f_n the number-average f. It is obvious that with increasing functionality the quality of the dendrimers deteriorates. However, even in the case of **3G-Vi** the polydispersity is extremely narrow, and the $f_{(dendrimer)}$ of **4G-Cl** is close to the theoretical value.

For the synthesis of the star polymers living PBLi with a molecular weight of 1000 g/mol was produced. The polydispersity was in all cases $M_w/M_n = 1.07$. Star polymers were synthesized by reacting the chlorosilane dendrimers **2G-Cl**, **3G-Cl**, and **4G-Cl** with an excess of PBLi. After 4 weeks of reaction time the mild promoter triethylamine was added, and the mixture was left for another 4 weeks to optimize the conversion. The excess of living PBLi over Si−Cl groups in the linking agents was 30, 40, and 100% for the synthesis of the 16-, 32-, and 64-arm stars, respectively. For comparison, a four-arm star was synthesized using $SiCl_4$ as the linking agent and an excess of 20% of PBLi. The reaction time in that case was 1 week. The MALDI-TOF MS spectrum of the four-arm star polymer **PB4-1** is given in Figure 2a. The differences between the signals of 54.1 mass units reflect the mass of one butadiene monomer unit. Table 2 gives the M_n found by MALDI-TOF MS. The result is in good agreement with the M_n determinated by vapor pressure osmometry (VPO). Additionally, $f_{(star)}$ calculated from $M_{n(star)}$(MALDI) and $M_{n(arm)}$(NMR) is very close to the theoretical value. The molecular weight distribution of the star, obtained from the MALDI-TOF MS measurement, is identical with the theoretical distribution, calculated from M_w/M_n of the arm and $f_{(theo)}$. These results along with the symmetrical shape of the MALDI-TOF MS signal indicate that within the experimental error a pure four-arm star was formed.

In the case of the star polymer **PB16-2** with 16 arms the quality of the linking agent is almost ideal (Table 1). The signal in the MALDI-TOF MS spectrum of the star (Figure 2b) is symmetrical in shape and shows a narrowly distributed material. The polymer character-

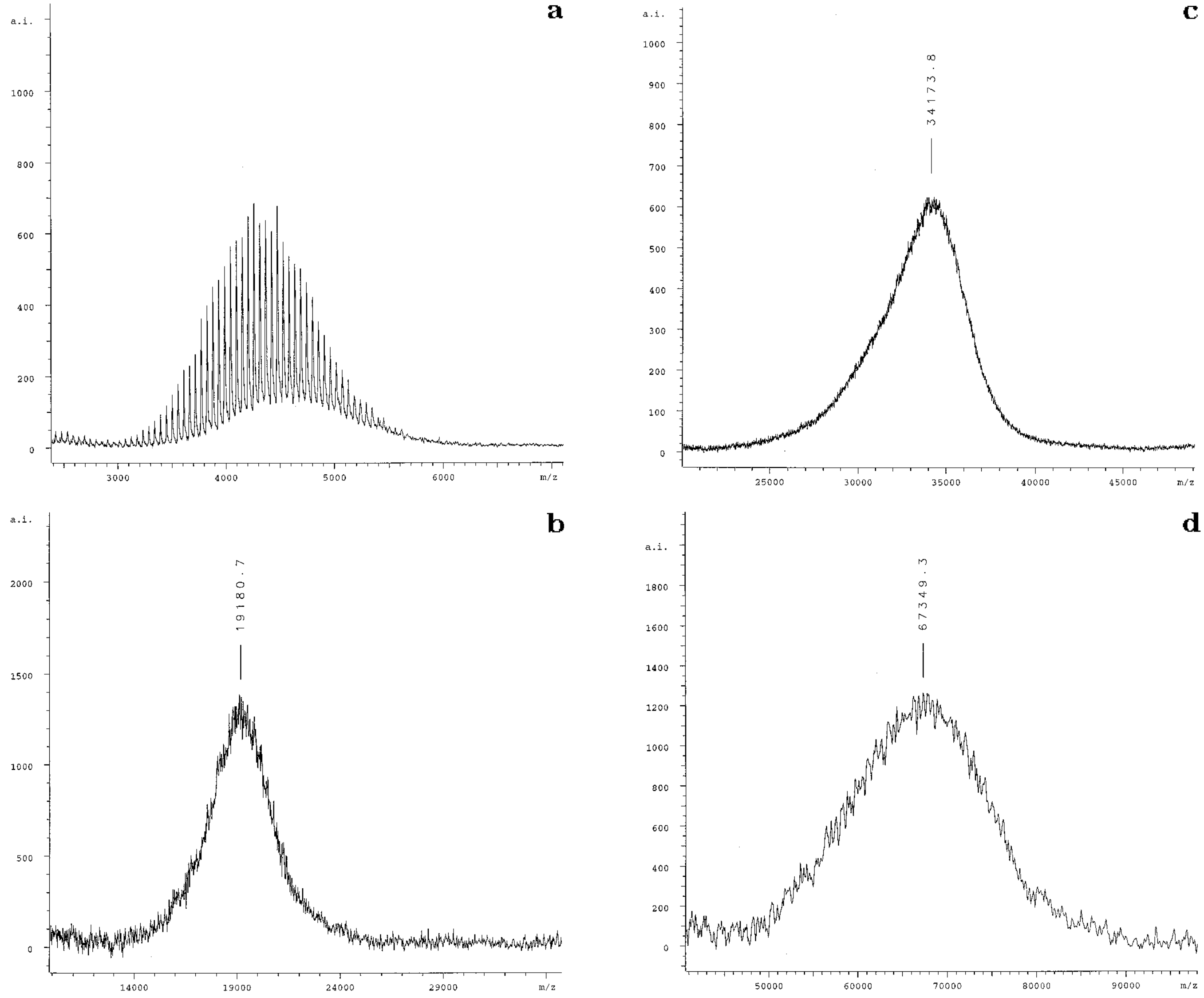

Figure 2. MALDI-TOF MS spectra of **PB4-1** (a), **PB16-2** (b), **PB32-1** (c), and **PB64-2** (d).

Table 2. Characterization of the Star Polymers

star polymer	$M_{n(star)}$ MALDI	$M_{n(star)}$ MO	$M_w/M_{n(star)}$ MALDI	$M_w/M_{n(star)}$ calcd[a]	$M_{n(arm)}$ NMR	$M_{(core)}$[b] calcd	$f_{(star)}$[c] MALDI/NMR
PB4-1	4 350	4 680[d]	1.02	1.02	1060	28	4.08
PB16-2	19 100	20 700	1.01	<1.01	1140	879	16.0
PB32-1	33 100	34 600	1.01	<1.01	1060	2014	29.3
PB64-2	66 300	68 600	1.02	<1.01	1140	4285	54.4

[a] Based on $M_w/M_{n(arm)}$, $f_{(star)}$ and $f_w/f_{n(dendrimer)}$. [b] $M_{(core)} = M_{(dendrimer)} - nM_{(Cl)}$ (n = 4, 16, 32, 64). [c] $f_{(star)} = (M_{n(star)}(\text{MALDI}) - M_{(core)})/M_{n(arm)}(\text{NMR})$. [d] VPO.

ization listed in Table 2 underlines this result. Again the values for M_n and M_w/M_n of **PB16-2** are in good agreement with the expected results. The ideal value for $f_{(star)}$ indicates complete conversion of the Si−Cl groups in the dendrimer.

However, the scenario starts to change for the star polymer **PB32-1** with 32 arms although the functionality of the corresponding chlorosilane dendrimer **3G-Cl** still is excellent. The MALDI-TOF MS signal of the star is visibly asymmetric. The strong tailing at the low molecular weight side clearly is a sign for incomplete conversion during the linking reaction. Although the very narrow distribution of $M_w/M_n = 1.01$ simulates a highly uniform material, the shape of the signal proves that this is not entirely the case. This finding is supported by the functionality of the star of 29.3, which is considerably smaller than the functionality of the linking agent with $f_{(dendrimer)} = 31$.

The MALDI-TOF MS spectrum for the 64-arm star **PB64-2** is given in Figure 2d. On one hand, the tailing at the low molecular weight side of the signal seems to be less pronounced than it is for the 32-arm star, but on the other hand, an additional tailing on the high molecular weight side appears. The second tailing is due to star material of higher functionality. Most likely, a trace of water causes the coupling of two chlorosilane dendrimers via a Si−O−Si bridge and is the source of some higher functional linking agent. The 16- and 32-arm stars do not contain detectable amounts of high molecular weight impurities. As the concentration of Si−Cl groups was similar for all star polymer synthesis, we can assume that also the ratio of water to Si−Cl groups was constant. However, the ratio of water to chlorosilane dendrimer molecules doubles with each generation, leading to a detectable amount of higher functional material, first, in the case of **PB64-2**. A weak high molecular weight tailing was also visible in the SEC signal of **PB64-2** and more pronounced in SEC signals of other star polymers that were produced using the same batch of linking agent. Therefore, an inclusion of matrix material from the MALDI-TOF MS sample preparation can be excluded for being responsible for the tailing.

Furthermore, the molecular weight characterization of **PB64-2** (Table 2) yields a considerably lower $f_{(\mathrm{star})}$ of 54.4 compared with the linking agent functionality of 60. The comparison of M_w/M_n with the calculated value for 100% conversion of the Si−Cl groups as well as the comparison with the 16- and 32-arm star characterization underlines the increased quality loss in the case of the 64-arm star.

To demonstrate the value and benefit of the MALDI-TOF MS investigation, in parallel experiments the star polymers were investigated by SEC. In all cases the signals were completely symmetrical in shape without showing any hint of other functionalities and indicated materials of very narrow distribution. This is due to the fact that for many-arm star polymers the hydrodynamic radius is almost independent of the arm number.

Prolonged reaction time might improve the completion of the linking event. For this reason samples that reacted 8 weeks were compared with samples taken after 4 weeks. Within experimental error the MALDI-TOF MS spectra were identical for both reaction times and all different stars. This fact also suggests that the addition of the promoter triethylamine after the first 4 weeks had no influence on the linking efficiency.

It still remains a question whether the results for the short-arm model stars are transferable to stars with $M_{n(\mathrm{arm})}$ 1 or more orders in magnitude larger. It seems logical that the increase in arm molecular weight reduces the efficiency of the linking reaction. However, according to the scaling model introduced by Daoud and Cotton, the density profile of a many-arm star polymer consists of three regions: an inner meltlike extended core region, an intermediate region resembling a concentrated solution, and an outer semidilute region.[21] For the linking reaction of the living chain ends the dominant barrier is the small inner section which is independent of $M_{n(\mathrm{arm})}$. Therefore, the maximum in conversion should not depend on the arm molecular weight if the reaction time is sufficiently long. Detailed membrane osmometry (MO) and low-angle laser light scattering experiments that we performed using PI 18-arm star polymers with $M_{n(\mathrm{arm})} = 7 \times 10^3$ and 2.5×10^4 g/mol as well as a 64-arm star polymer with $M_{n(\mathrm{arm})} = 1 \times 10^4$ g/mol support this model and confirm the results of the short-arm stars. The 18-arm stars showed ideal arm numbers. and the measured functionality of the 64-arm star was approximately 55. The functionalities of many-arm star polymers reported in the literature even tend to be higher than the values we report in this paper.[6,22] The former results, however, were obtained calculating $f_{(\mathrm{star})}$ by the use of M_w from light scattering measurements, which leads to relatively higher functionalities.

In conclusion, the detailed investigation of PB short-arm star polymers by MALDI-TOF MS reveals that up to functionality 16 the quality of the linking agent as well as the star polymer itself is almost ideal with respect to functionality as well as polydispersity. The loss of quality for higher functionalities is partly due to the linking agent and partly caused by an incomplete coupling reaction of living polymer chain ends with the Si−Cl groups of the dendrimers. This incomplete reaction is explained sterically. As the space per reactive group on the dendrimer surface is decreasing with each generation, the coupling reaction is getting more hindered with increasing functionality.

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