One-Pot Synthesis of Arborescent Polystyrenes

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ABSTRACT: A new grafting-from procedure was developed for the synthesis of arborescent styrene polymers of successive generations in a single reaction pot. Styrene was first copolymerized anionically in a semibatch process with 1,3-diisopropenylbenzene (DIB), and the chains were terminated with methanol. The pendent isopropenyl moieties of the DIB units were then reacted with *sec*-butyllithium to generate a polyfunctional anionic macroinitiator. Further additions of styrene−DIB monomer mixture to the activated linear substrate yielded a comb-branched (generation G0) copolymer. After termination of the chain ends and activation of the double bonds on the G0 substrate, styrene monomer was added to generate G1 arborescent polystyrenes, with a dendritic architecture. Alternately, the G0 copolymer was isolated by precipitation and activated in a separate procedure. The size (molecular weight) of the side chains in the G1 polymer was conveniently controlled by varying the amount of monomer added to the G0 macroinitiator. The reaction conditions were optimized to obtain graft polymers with relatively low polydispersity indices ($M_w/M_n = 1.1-1.3$) and absolute weight-average molecular weights M_w reaching 7×10^6. The intrinsic viscosity in toluene of the arborescent G1 polystyrenes synthesized was up to 7.2 times lower than for linear polystyrene samples of comparable molecular weight.

Introduction

Dendritic macromolecules, characterized by a molecular architecture with multiple branching levels, are comprised of three branched polymer families: dendrimers, hyperbranched polymers, and dendrigraft (or arborescent) polymers.[1] Compounds in the first two categories are typically derived from small molecules in either strictly controlled (dendrimers) or random (hyperbranched polymers) branching reactions, while arborescent polymers are usually assembled from linear polymer chains in successive grafting reactions. Most arborescent polymers have been synthesized by anionic polymerization whereby a linear polymer is first randomly functionalized with coupling sites and reacted with “living” anionic polymer chains to yield a comb-branched (generation G0) structure. Further functionalization and grafting cycles lead to upper generation (G1, G2, etc.) arborescent polymers with a dendritic architecture (Figure 1). The most significant advantage of this strategy is that a high molecular weight is attained in very few steps. Chloromethyl[2] and acetyl[3] functionalities were thus introduced on polystyrene as coupling sites for the synthesis of arborescent polystyrenes. Other “living” macroanions including poly(2-vinylpyridine)[4] and polyisoprene[5] were likewise grafted onto polystyrene backbones to obtain arborescent copolymers. In a related procedure, chlorodimethylsilyl functionalities were used as coupling sites for the synthesis of arborescent polybutadienes.[6] Despite the rapid molecular weight growth observed for successive generations, the arborescent polymer syntheses reported so far require multiple steps of substrate functionalization, polymerization, grafting, and purification. For this reason, it is important to develop shorter pathways for the synthesis of dendritic graft polymers.

A one-pot convergent scheme suggested by Knauss et al.[7,8] for the synthesis of dendrigraft polymers is based on simultaneous anionic polymerization and grafting reactions of styrene homo- and copolymers with either 4-chloromethylstyrene or 4-chlorodimethylsilylstyrene acting as both coupling agents and monomers. The anionic propagating center at the focal point (active center) of the graft polymer quickly becomes sterically hindered by the surrounding side chains in this approach. Furthermore, the S_N2 termination reaction between the anionic propagating centers and the coupling sites is much faster than propagation. For these reasons, it is difficult to obtain polymers with both a high molecular weight and a high branching density under these conditions. The self-condensing anionic copolymerization of styrene and 1,3-diisopropenylbenzene (DIB) was also recently investigated by Baskaran[9] to synthesize hyperbranched polystyrenes. The branched polymers obtained were characterized by very broad molecular weight distributions ($M_w/M_n = 2-17$) and relatively low molecular weights due to early termination of the reaction that was necessary to avoid intermolecular cross-linking (gelation) under the conditions used. The one-pot atom transfer radical copolymerization of styrene and a 4-chloromethylstyrene “inimer” (initiator monomer) was likewise explored to synthesize hyperbranched polystyrenes and comb-branched polystyrene-*graft*-poly(ethyl methacrylate).[10] These methods were also limited by the occurrence of cross-linking, in addition to difficulty in separating the catalyst from the final product. The cationic copolymerization of isobutene with an inimer such as 4-(2-methoxyisopropyl)styrene similarly provided a one-pot method to synthesize hyperbranched polyisobutylenes,[11] this approach being limited to cationically polymerizable monomers.

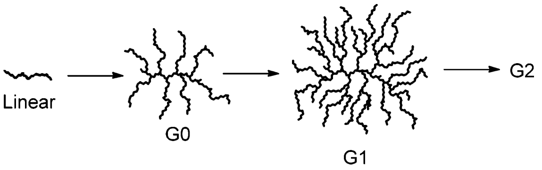

Figure 1. Schematic representation of the arborescent polymer synthesis.

The synthesis of comb-branched polymers according to an anionic grafting-from strategy was investigated by Lutz et al.[12] In this case a copolymer of α-methylstyrene and 1,3-diisopro-

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penylbenzene was synthesized by anionic copolymerization at low conversion, purified from unreacted monomer by precipitation, and activated with 20−30% excess *sec*-butyllithium before adding styrene monomer to grow side chains from the linear substrate. The graft polymers had polydispersity indices (PDI = M_w/M_n) ranging from 1.2 to 2.5, apparently due to cross-linking reactions occurring during substrate activation and side-chain growth.

In this paper, a one-pot method is described for the synthesis of arborescent polystyrenes based on the semibatch copolymerization of styrene and 1,3-diisopropenylbenzene to high conversion. Activation of the pendent double bonds in the copolymer is achieved with *sec*-butyllithium without isolation of the substrate. Repetition of the copolymerization and double bond activation steps allows the synthesis of arborescent polymers of generation G1. The solution properties of arborescent polystyrenes derived from a one-pot method are compared with those of linear polystyrenes and arborescent polystyrenes synthesized from successive (stepwise) functionalization and grafting reactions.

Experimental Section

Solvent and Reagent Purification. The solvents and reagents serving in the reactions were purified by inert atmosphere and vacuum techniques standard for anionic polymerization. The detailed conditions used are provided as Supporting Information.

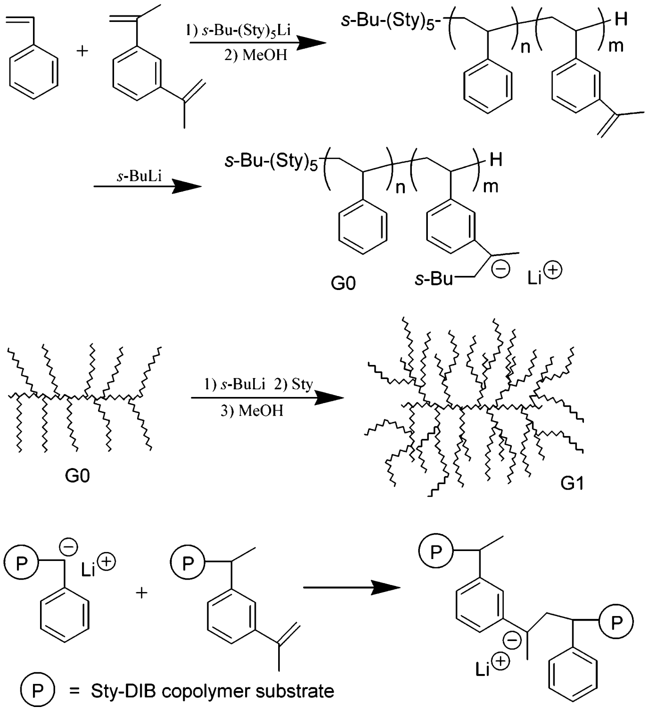
Synthesis of Linear Styrene−DIB Copolymer. The reaction conditions specified are those providing optimal results (sample L-5). A 1 L five-neck round-bottomed flask with a magnetic stirring bar was attached to the high-vacuum line, before mounting toluene and THF supply lines from purification stills, a LiCl ampule (1.40 g, 33 mmol in 50 mL of THF; subsequently used in the synthesis of the G1 polymer), and a rubber septum. The flask was flamed under high vacuum and filled with purified nitrogen. After cooling, toluene from the drying still (20 mL) was added as well as one drop of styrene from a syringe. The solvent was titrated with a *sec*-butyllithium solution (*s*-BuLi; Aldrich, 1.35 M in cyclohexane) to give a persistent light yellow color. Additional *s*-BuLi (0.18 mL, 0.24 mmol) was then injected into the reactor, followed by 0.14 mL of styrene (0.13 g, 1.2 mmol, for a calculated number-average degree of polymerization $X_n = 5$). After 20 min, the flask was cooled to −78 °C and THF (40 mL) was added. After 10 min, the semibatch addition of 1.40 g (12.0 mmol, 1.54 mL) of the styrene−DIB mixture (3:1 mole ratio, for an average $X_n = 50$) from a gastight syringe was initiated and completed over a period of 16 min. For each addition, a 0.13 mL aliquot of the monomer mixture (corresponding to 0.72 mmol of styrene and 0.24 mmol of DIB) was injected and allowed to react for 80 s. This led to color changes alternating between yellow and brown within a few seconds of each addition. After complete addition of the monomer mixture the reaction was continued at −78 °C with stirring for 1 h, while removing 0.3 mL samples every 15 min for size exclusion chromatography (SEC) and gas chromatography (GC) analysis. The reaction was then terminated by titration with nitrogen-purged 10:1 THF−methanol to just reach the (colorless) end point. A 30 mL aliquot of the polymer solution (out of a total residual volume of ca. 60 mL) was removed through the septum. The copolymer was recovered by precipitation in methanol, dried under vacuum for 24 h (0.72 g, 95% yield), and analyzed by SEC (apparent $M_n = 7500$, $M_w/M_n = 1.32$ based on a linear polystyrene standards calibration curve) and ^{1}H NMR spectroscopy.

G0 (Comb-Branched) Styrene−DIB Copolymer. The reaction conditions specified are those providing optimal results (sample G0-5b). The reaction mixture remaining in the flask after the synthesis of the linear copolymer (30 mL of solution, 0.76 g of copolymer) was diluted to 300 mL with purified THF and cooled to −20 °C with an ice−methanol bath. The mixture was titrated with *s*-BuLi to a light brown color, and 1.35 mmol of *s*-BuLi (1.0 mL, for 24% reaction of the substrate based on the monomer mixture used, 95% reaction based on DIB units alone) was added to produce initiating sites along the linear polymer substrate. After 4 h the reaction mixture was cooled to −78 °C, and 8.0 g (68 mmol, 8.8 mL) of the styrene−DIB mixture (3:1 mole ratio, for a calculated side chain $X_n = 50$) was added using a semibatch addition protocol (0.6 mL aliquot additions followed by about 2 min waiting) over 30 min and produced color changes as described above. After complete addition of the monomer mixture the reaction was continued for 1 h, and samples were removed from the reactor after 5 and 30 min for analysis by SEC and GC. The reaction was terminated by titration with a 10:1 THF−methanol mixture. Two-thirds (200 mL) of the reaction mixture was then removed from the reactor. The G0 copolymer was recovered by precipitation in methanol, dried under vacuum for 24 h (5.7 g, 97% yield), and analyzed by SEC (apparent $M_n = 5.6 \times 10^4$, $M_w/M_n = 1.68$), SEC-MALLS (absolute $M_n = 8.1 \times 10^4$, $M_w/M_n = 1.73$), and ^{1}H NMR spectroscopy.

Synthesis of G1 Arborescent Polystyrene. The G0 styrene−DIB copolymer remaining in the flask (2.9 g of polymer in 100 mL of THF) was diluted with 400 mL of THF. The solution was titrated with *s*-BuLi to a light brown color, before adding 5.4 mmol of *s*-BuLi (4.0 mL, for 24% reaction based on the styrene and DIB units in the copolymer, 95% reaction based on DIB units alone). After activation at −20 °C for 4 h the flask was cooled to −78 °C, and LiCl was added from the ampule (1.40 g in 50 mL of THF, 6 equiv with respect to initiator) as well as 27 g of styrene (for a calculated side chain $M_n = 5000$) using a syringe. After 2 min the polymerization was terminated with degassed methanol. The polymer (sample G1-5b) was recovered by precipitation in methanol, dried under vacuum (29.3 g, 99% yield), and purified by precipitation fractionation in toluene/methanol. The purified polymer was analyzed by SEC (apparent $M_n = 6.0 \times 10^5$, $M_w/M_n = 1.22$), MALLS ($M_n = 1.3 \times 10^6$, $M_w/M_n = 1.22$), and ^{1}H NMR spectroscopy.

Synthesis of Analogous Arborescent Polystyrene Series by Chain Extension. The synthesis of a series of arborescent G1 polystyrenes differing in side-chain molecular weight (2500, 5000, 10 000, 20 000) and having the same branching functionality was achieved by successive monomer additions. Because of the high solution viscosity of branched polymer samples with long side chains, the reaction was preferably carried out in a 2 L five-neck glass reactor equipped with a vacuum-tight mechanical stirrer, using a G0 copolymer substrate isolated by precipitation. The synthesis of the G0 styrene−DIB copolymer used in the reaction was conducted as described above ($M_n = 1.1 \times 10^5$, $M_w/M_n = 1.69$, styrene:DIB = 3). The THF inlet from the still, a styrene ampule (41.5 mL of styrene in 375 mL of THF), a LiCl ampule (1.0 g, 24 mmol in 50 mL of THF), a sampling tube, and a septum were mounted on the reactor, which was flamed under high vacuum, cooled to room temperature, and filled with nitrogen. The dry G0 copolymer (1.50 g) was then loaded in the reactor and dried further under high vacuum for 30 min. After filling the reactor with nitrogen and cooling to −20 °C, the copolymer was dissolved in 400 mL of THF and titrated with *s*-BuLi to a light brown color. Additional *s*-BuLi was then injected in the reactor (3.6 mmol, 2.7 mL, for 27.5% reaction based on the styrene and DIB units in the copolymer, 10% excess based on DIB units alone). After 4 h of activation at −20 °C the reaction mixture was cooled to −78 °C and LiCl was added, followed by 90 mL of the styrene−THF solution over 5 min (8.1 g of styrene, for a target side chain $M_n = 2500$). A quick color change from brown to yellow was observed. After polymerization for 10 min at −78 °C, an aliquot of polymer solution (185 mL, 3.5 g of polymer) was transferred through the sampling tube into a nitrogen-purged graduated funnel containing 0.5 mL of degassed methanol. After a second styrene solution addition (66.5 mL, 6.0 g of styrene, for a total side chain target $M_n = 5000$) and 20 min waiting, 115 mL of polymer solution (3.5 g of polymer) was removed and terminated as above. A third aliquot of styrene solution (96 mL, 8.7 g of monomer, for a total side chain target $M_n = 10\,000$) was added. After 30 min, 78 mL of polymer solution

Scheme 1. One-Pot Synthesis of G1 Arborescent Polystyrenes and Side Reaction Leading to Cross-Linking



(3.5 g of polymer) was removed and terminated. A fourth aliquot of styrene solution (158 mL, 14.2 g of monomer, for a total side chain target $M_n = 20\,000$) was added. After 40 min, the polymerization was terminated by injecting degassed methanol into the reactor. All samples were recovered by precipitation in methanol and characterized by SEC. The crude graft polymers were purified by precipitation fractionation in toluene/methanol to remove linear polystyrene contaminant and analyzed by SEC-MALLS. Analogous G0 polystyrene samples were synthesized by a similar procedure, starting from a linear styrene−DIB copolymer substrate ($M_n = 8.3 \times 10^3$, $M_w/M_n = 1.50$, styrene:DIB = 3, 1.50 g) and a solution of styrene (41.8 mL) in THF (380 mL; 10% v/v).

Polymer Characterization. Apparent (polystyrene-equivalent) and absolute molecular weight data (M_n, M_w, and PDI = M_w/M_n) were determined by size exclusion chromatography (SEC) analysis. Viscosity measurements were made in toluene at 25.0 ± 0.2 °C. Detailed procedures for both types of measurements are provided as Supporting Information. ^{1}H NMR analysis was performed on a Bruker AM-300 nuclear magnetic resonance spectrometer. The polymers were dissolved in $CDCl_3$ at a concentration of 5% w/v.

Results and Discussion

The strategy used for the synthesis of arborescent polymers using DIB is described in Scheme 1 and relies on the much lower reactivity of the second isopropenyl group of DIB toward the propagating centers.[12,13] A detailed discussion of structure−reactivity relations among the different monomers and propagating species involved in the reaction is provided as Supporting Information. The most important side reaction leading to molecular weight distribution (MWD) broadening, due to the attack of a living chain end onto a pendent double bond of a DIB unit on a different substrate molecule, is also depicted at the bottom of Scheme 1. After reaching a high (>99%) conversion in the synthesis of the linear styrene−DIB copolymer, the living chains are terminated by titration with methanol and the pendent isopropenyl moieties are activated with *s*-BuLi to generate initiating sites. The addition of styrene and DIB to the lithiated macroinitiator yields a G0 copolymer. Further activation of the G0 substrate and styrene monomer addition produces a G1 arborescent styrene polymer. The results obtained for the synthesis of G0 styrene−DIB copolymers and of G1 arborescent polystyrenes are summarized in Tables 1 and 3, respectively, and will be discussed in detail below. Sample labeling for the reaction products starts with L (linear), G0, or G1 to identify the generation number, followed by a run (attempt) number. For example L-2, G0-2, and G1-2 refer to successive generations derived from the same one-pot reaction. An additional letter is sometimes used to identify different samples derived from the same precursor under different conditions. Thus, samples G0-5a and G0-5b were obtained by splitting the L-5 precursor in two equal portions and diluting it to different extents for the synthesis of the G0 samples.

Optimization of the Reaction Conditions for the Synthesis of the Linear Styrene−DIB Copolymers. The conditions used for the preparation of the linear copolymers were optimized in terms of the initiation method, the reaction temperature, and the monomer addition protocol used. To focus on the synthesis of the branched polymers, only a brief summary of these results is provided here. A detailed discussion of the optimization procedures and full characterization results for the linear copolymers are supplied as Supporting Information. Further optimization of the reaction conditions necessary for the synthesis of the G0 and G1 polymers is discussed subsequently.

The copolymerization reaction was initiated with oligostyryllithium rather than *s*-BuLi because of its greater selectivity toward the first double bond of DIB. To minimize the amount

Table 1. Optimization of Reaction Conditions for the Synthesis of G0 Styrene−DIB Copolymers[a]

			monomer addition						
sample	St:DIB[b]	THF/mL	method	time/min	polym time[c]/min	M_n SEC[d]/10^3	M_n MALLS[e]/10^3	M_w/M_n[d]	residual DIB/%
G0-1	3	200	dropwise	30	30	71		1.73	∼3
G0-2	3	200	dropwise	40	30	71		1.88	∼1
					60	73		2.04	
G0-5a	3	200	semibatch	34	30	52	79	1.66	∼1
					60	55		1.77	
G0-5b	3	300	semibatch	37	30	55	81	1.61	∼1
					60	56		1.68	
G0-7a	2.5	300	semibatch	37	30	55	87	1.66	∼1
					60	60		1.74	
G0-7b	2.5	300	semibatch	38	30	56	91	1.65	∼1
					60	62		1.86	<1
					120	67		2.16	
G0-8	3.5	300	semibatch	30	30	50	77	1.68	<1
					60	56		1.78	

[a] Linear polymers activated for 4 h at −20 °C with *s*-BuLi, G0-1 polymerization at −35 °C, other reactions at −78 °C, 50 equiv styrene−DIB monomer mixture used. [b] Styrene:DIB monomer ratio used in the reaction. [c] Polymerization time allowed after completing monomer addition. [d] Apparent value based on linear polystyrene calibration. [e] Absolute value determined using MALLS detector.

Table 2. Determination of Optimal Styrene−DIB Copolymer Activation Conditions[a]

substrate	St:DIB[b]	activator	temp/°C	time/h	linear PS/wt %
L-1	3	*s*-BuLi	−78	6	3
L-1	3	*s*-BuLi	−20	4	0
L-1	3	*t*-BuLi	−20	4	0
L-1	3	*n*-BuLi	−20	4	4
L-6	2.5	*s*-BuLi	−20	4	0
G0-5b	3	*s*-BuLi	−20	4	0
G0-7a	2.5	*s*-BuLi	−20	4	<1
G0-7b	2.5	*s*-BuLi	−20	5	0

[a] Linear (L) and G0 copolymer substrates precipitated to eliminate residual monomer, 95% activation based on DIB content. [b] Styrene:DIB monomer ratio in copolymer.

of residual DIB present, a temperature of −78 °C was selected for the copolymerization reaction. A batchwise monomer addition protocol was employed to ensure a uniform distribution of DIB units within the styrene−DIB copolymer (vide infra).

Monomer Addition Protocol. Two different monomer addition protocols were investigated to compensate for the fast polymerization rate of styrene as compared to DIB and to minimize the occurrence of cross-linking reactions. The first method examined used dropwise addition of the monomer mixture until the yellow coloration of polystyryl anions was observed and waiting for a few seconds until the dark brown coloration of the DIB anions reappeared before the next addition. In the second method (semibatch addition), described in the Experimental Section, the addition of each monomer mixture aliquot corresponding to ca. 3 equiv of styrene and 1 equiv of DIB per living end was followed by a longer (80−120 s) delay before the next addition, to allow the incorporation of a DIB unit at the chain end. This approach, apart from achieving a more uniform distribution of branching points along the substrate, also yielded superior results in terms of PDI and reproducibility as compared with dropwise addition of the monomer mixture. The average spacing between branching points (DIB units) is expected to be 3 styrene units on average by this method (for a 3:1 styrene:DIB ratio). However, because of the fast propagation rate of styrene in anionic polymerization and diffusion limitations, the actual spacing between branching points may vary in practice.

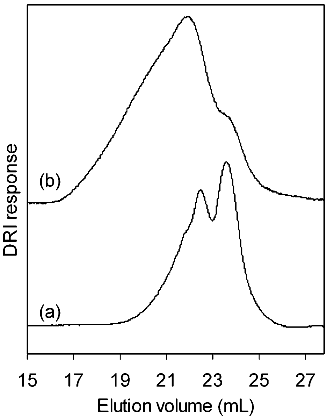


Figure 2. Influence of monomer addition protocol on the SEC elution curves of G0 styrene−DIB copolymers with styrene:DIB ratio = 3 and post-addition polymerization time of 1 h: (a) semibatch addition (G0-5a); (b) dropwise addition (G0-2).

The influence of the monomer addition protocol on the PDI was rather limited for linear copolymer substrates (see Supporting Information), but it was much more significant for the synthesis of the G0 copolymers. The characterization results obtained for samples G0-2 and G0-5a (Figure 2 and Table 1) clearly show that the semibatch addition protocol yields lower PDI values than dropwise addition for the G0 copolymers. It is also obvious from the SEC traces of Figure 2, obtained for a fixed post-addition polymerization time of 1 h, that the semibatch protocol produces less dimerization and multimerization (cross-linking) for the G0 copolymers than dropwise addition. The average PDI and standard deviation values (SD, given between parentheses) obtained for successive G0 copolymer syntheses with a styrene:DIB monomer ratio of 3 and a 1 h post-addition polymerization time are: for semibatch addition 1.8_1 (0.13) over eight runs; for dropwise addition, 2.4_2 (0.39) over five runs.

Semibatch addition clearly yielded lower PDI values and less variability in the synthesis of the G0 copolymer. Additionally, semibatch addition is more likely to produce copolymers with a uniform distribution of DIB units. On the basis of these results, batchwise addition was the preferred monomer addition protocol.

Post-Addition Polymerization Time. The reaction time allowed after the completion of monomer additions affects both the monomer conversion and the PDI obtained (due to the cross-linking reactions). Analysis of the reaction mixture by SEC and GC confirmed that 5 min after completing the monomer additions the target molecular weight was attained in the synthesis of the linear copolymer irrespective of the monomer addition protocol used; however, small amounts of residual DIB were still present in the reactor. Residual DIB is undesirable because it would react with *s*-BuLi in the subsequent copolymer activation step and form linear polymer contaminant in the synthesis of higher generation polymers. This is seen, for example, as a small peak at an elution volume of ca. 27 mL in Figure 3a. While a longer polymerization time should improve the DIB conversion attained, it may also favor cross-linking via attack of the pendent isopropenyl moieties by the anionic propagating centers,[12] as shown at the bottom of Scheme 1. In the synthesis of linear and G0 copolymers, styrene was undetectable by GC analysis 5 min after completing monomer addition. For the linear copolymer, ca. 1% of the total DIB

Table 3. Synthesis of G1 Polystyrenes by a True One-Pot Process[a]

				M_n/10^6				
sample	G0 St:DIB[b]	BuLi:DIB[c]	time[d]/min	SEC[e]	MALLS[f]	calcd[g]	M_w/M_n[f]	linear PS/%
G1-1	3	0.95	2	0.59			1.20[e]	31
			10	gel				
G1-5a	3	0.95	2	0.61	1.4	0.90	1.25	9
G1-5b	3	0.95	2	0.60	1.3	0.90	1.22	9
G1-7a	2.5	0.95	2	0.66	1.8	0.99	1.23	10
G1-7b	2.5	0.95	2	0.73	2.5	1.2	1.24	4
G1-8	3	1.1	30	0.63	1.4	0.95	1.23	14

[a] G0 polymer activated for 4 h at −20 °C, 95% activation based on DIB content, target side chain M_n = 5000, polymerization at −78 °C. [b] Mole ratio of styrene to DIB in G0 copolymer substrate. [c] Mole ratio of activating compound to isopropenyl units based on DIB content. [d] Polymerization time after monomer addition. [e] Apparent value based on linear polystyrene calibration. [f] Absolute value determined using MALLS detector. [g] Calculated M_n based on reaction mass balance.

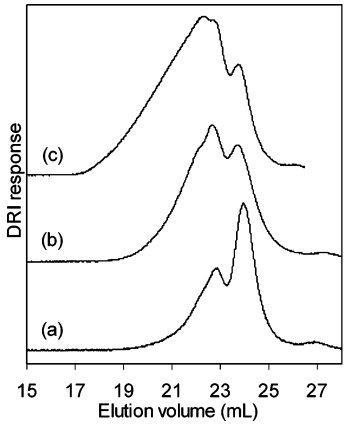


Figure 3. Influence of post-addition polymerization time on the SEC elution curves of G0 copolymer with styrene:DIB ratio = 2.5 for sample G0-7b after (a) 30 min, (b) 1 h, and (c) 2 h.

amount added was still present after 30 min, and no monomer was detected after 60 min. For the G0 copolymers, 3% monomer was detected after 30 min and ca. 1% after 1 h. This result suggests that the propagating centers in the G0 copolymer are less reactive than in the linear substrates. The decreased reactivity could be due to association, in analogy to the intermolecular association effects observed for small molecule organolithium initiators.[14]

For linear copolymer samples, the increase in apparent M_n and PDI was noticeable after 60 min and even more significant after 2 h (see Supporting Information). For the G0 copolymer synthesis the PDI increased even faster than for the linear polymer in the post-polymerization stage because of the higher molecular weight of the substrate and its greater susceptibility to cross-linking reactions. The SEC elution curves obtained for samples removed from reaction G0-7b 30 min, 1 h, and 2 h after completing monomer addition are compared in Figure 3. While the conditions used for these samples are somewhat different from the ones discussed up to this point (styrene:DIB ratio = 2.5 and lower living end concentration), the curves display an evolution of the MWD typical of all reactions. The growth of a broad second peak is observed at an apparent molecular weight (110 000) almost twice as large as the main peak centered around 62 000. The higher molecular weight peak increases in intensity and broadens with time, a poorly resolved shoulder (corresponding to multimerization) being apparent after 1 h.

A compromise is clearly necessary between minimizing the amount of unreacted DIB forming linear polymer contaminant and obtaining a reasonably low PDI, by varying the post-addition polymerization time. The influence of polymerization time on the synthesis of G1 polymers will be discussed using samples G0-7a and G0-7b, based on the same linear (L-7) substrate but subjected to different polymerization times for the G0 sample (vide infra).

Monomer Ratio. The styrene:DIB monomer ratio used in the reaction determines the branching density of the graft polymers. Previous results have shown[15] that a branching density (fraction of monomer units acting as branching sites) of 20−30% on a polystyrene backbone is sufficient to obtain rigid-sphere-like behavior in solution. This corresponds to a styrene:DIB ratio in the range of about 4−2.5, assuming that all pendent double bonds on the copolymer become branching points. For G0 copolymers G0-7b, G0-5a, and G0-8 (Table 1) and their linear precursors (see Supporting Information), styrene:DIB ratios of 2.5, 3, and 3.5 were used in the reactions, respectively.

The monomer ratio, while influencing molecular rigidity, may also affect side reactions. For example, at low styrene:DIB ratios the difunctional monomer may have a higher tendency to accumulate in the reactor. Slower addition and/or a longer post-addition polymerization time may be necessary to attain a high DIB conversion, thus increasing the probability of cross-linking. A sensitive indicator of the presence of residual monomer is the amount of linear polymer contaminant generated in the subsequent grafting reaction. The SEC elution curves for G0 copolymers using styrene:DIB ratios of 3 and 2.5, following a post-addition polymerization time of 1 h, are represented in Figures 2a and 3b, respectively.

The copolymer generated at the higher styrene:DIB ratio (lower DIB concentration) has no detectable amount of linear polymer, but a small peak corresponding to linear contaminant is visible in Figure 3b (styrene:DIB = 2.5) at an elution volume of about 27 mL. The PDI values obtained are comparable for the G0 copolymers (Table 1) and the linear copolymers (see Supporting Information) when the styrene:DIB ratio is varied within the range 2.5−3.5.

Activation Time. Different butyllithium isomers (*n*-BuLi, *s*-BuLi, and *t*-BuLi) were investigated to activate the pendent isopropenyl groups of the styrene−DIB copolymers and generate initiating sites (Table 2). To eliminate interferences due to residual DIB, precipitated linear and G0 copolymers were used to examine the influence of the contact time, the temperature, and the structure of the organolithium compound on the reaction. In each case an activation level of 95% based on the DIB units content was targeted, to minimize the generation of linear polymer due to excess organolithium activating compound. After a preset activation time (4−6 h) the lithiated polymer was used to initiate the polymerization of styrene, to verify whether linear polymer was generated due to unreacted BuLi. The amount of linear polymer formed was quantified as a wt % content in the product, from the relative peak areas for the graft polymer and the linear component (Table 2).

Because THF can be attacked by organolithium compounds (*t*-BuLi in particular) at higher temperatures,[16] it is preferable to carry out the activation reaction at or below −20 °C. For *s*-BuLi the color change (from colorless to brown) characteristic of site activation was instantaneous at −20 °C but required ca. 1 s at −78 °C.

The addition of *s*-BuLi to the pendent isopropenyl moieties of the linear copolymer was complete after 4 h at −20 °C but incomplete even after 6 h at −78 °C, as indicated by the generation of 3% linear polystyrene in the reaction. Both *s*-BuLi and *t*-BuLi gave a faster color change than *n*-BuLi when added to the linear styrene-DIB copolymers at −20 °C. After 4 h both *s*-BuLi and *t*-BuLi reacted completely, since no linear polymer was generated (Table 2). For the G0 copolymer with a styrene:DIB ratio of 2.5 (last two entries of Table 2) the activation time had to be increased slightly to avoid linear polymer generation, possibly due to increased charge repulsion along the chains. Small (5 mL) samples of the activated G0 polymer solutions were removed from each reaction before monomer addition and deactivated with methanol for SEC analysis. The PDI of the polymers increased by about 0.1 unit in all cases, which implies that minimal cross-linking occurred even though the isopropenyl pendent groups were present in excess. This is presumably because the reactive centers generated are hindered and unreactive toward isopropenyl moieties and because the activation reaction was conducted at a relatively low concentration (0.4−0.7% w/v).

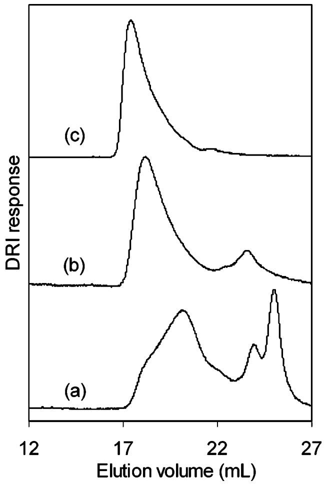


Figure 4. Influence of post-addition polymerization time in the G0 polymer synthesis on the generation of linear polymer contaminant in the G1 polymer synthesis: (a) G1-1, 30 min G0 polymerization; (b) G1-7a, 1 h G0 polymerization; (c) G1-7b, 2 h G0 polymerization.

Effects of Polymer Concentration, Lithium Salt Modifiers, and Substitution of 1,3-DIB with 1,4-DIB. The potential influence of these parameters on the grafting reaction was investigated but found to be negligible in most cases. The results obtained in these experiments are provided as Supporting Information. The addition of LiCl in the synthesis of the G1 styrene polymers was nonetheless found to be beneficial, as it reduced the viscosity of the reaction mixture and avoided gel formation in the presence of excess isopropenyl groups (substoichiometric activation, vide infra).

Synthesis of Styrene Arborescent Polymers. The true one-pot synthesis of arborescent polystyrenes of overall generation G1 was achieved by initiating the polymerization of styrene with the activated G0 styrene−DIB copolymer. The results obtained for the synthesis of polymers with a target side chain $M_n = 5000$ using macroinitiators with an activation level of 95% based on isopropenyl units content (substoichiometric activation) are reported in Table 3. The amount of linear polymer generated in the reactions, as determined by SEC analysis of the products, is provided in the last column. The influence of the post-addition polymerization time used in the synthesis of the G0 substrate on the amount of linear polymer generated is also illustrated in Figure 4. Since the activation conditions for the G0 substrate were the same as in the model reactions (using precipitated polymer), linear polymer generated in the one-pot reactions can be attributed unambiguously to the presence of residual DIB. Some of the living chains generated by the reaction of DIB with the *s*-BuLi used to activate the copolymer substrate may potentially graft onto the residual double bonds on the substrate in the case of substoichiometric activation and thereby decrease the amount of linear contaminant in the product. Grafting has indeed been achieved by reacting polystyryl anions with DIB copolymers in the presence of THF for an extended time period (2−12 h) at 35 °C.[12] This possibility cannot be ruled out since the one-pot procedures involved a total reaction time of ca. 8−9 h for the G1 polymers, but it may not be very significant due to the lower temperature used (−20 °C).

Sample G1-1 (Figure 4a, derived from G0-1 with 30 min post-addition polymerization) contained as much as 31% linear polymer contaminant. The linear contaminant (at elution volumes above 23 mL) has a bimodal distribution due to the reaction of either one or both isopropenyl moieties of DIB with *s*-BuLi in the activation step. Samples G1-5a,b and G1-7a,b, all synthesized from the corresponding G0 substrates described in Table 1 at least 60 min after the monomer mixture addition was completed, contained 4−10% linear contaminant (Table 3). Samples G1-7a (Figure 4b) and G1-7b (Figure 4c) were synthesized from substrates G0-7a (1 h post-addition polymerization time) and G0-7b (2 h polymerization time), respectively (Table 1). A longer polymerization time in the G0 substrate preparation yields less linear polymer in the G1 sample synthesis (Table 3), but also increases cross-linking and the PDI of the G0 products (Table 1). A compromise must be drawn between producing less linear polymer and attaining a low PDI value for the G0 polymer.

A problem specific to the synthesis of G1 arborescent polystyrenes (due to their higher molecular weight) is their increased sensitivity to the attack of residual isopropenyl moieties by the polystyryllithium propagating centers, potentially leading to cross-linking or gelation. The addition of pure styrene monomer to the activated G0 substrate without LiCl led to gelation of the reaction mixture in less than 1−2 min with substoichiometric activation. This problem was minimized by adding LiCl to the reaction to decrease the reactivity of the propagating centers: No gelation was observed for reactions in the presence of 6 equiv LiCl over a few minutes; the reactions were terminated 2 min after monomer addition as a precaution. Another strategy to avoid cross-linking (applied in the chain extension procedure discussed below) is the use of an excess of *s*-BuLi in the activation reaction to ensure the full consumption of the pendent isopropenyl moieties. This approach is illustrated by sample G1-8 in Table 3, synthesized with 10% excess *s*-BuLi. No gelation was observed even 30 min after styrene addition, but the amount of linear polymer generated increased to 14% as compared to 4−10% for most other reactions with substoichiometric activation.

A comparison of Table 3 with Table 1 shows that even though the G0 substrates used in the reactions had polydispersity indices above 1.6, the G1 polymers all had $M_w/M_n \leq 1.25$. This phenomenon was also observed in the synthesis of G0 and G1 polystyrenes with different side chain lengths in the presence of excess *s*-BuLi (Table 4) and will be discussed subsequently.

Side-Chain Extension Reactions. In the proposed grafting-from scheme the molecules grow outward from the substrate, and the propagating centers should remain “living” (reactive) unless impurities are present or side reactions occur. The synthesis of two analogous series of G0 and G1 arborescent polystyrenes with different side-chain molecular weights and the same branching functionality can be achieved by successive monomer additions, if it is assumed that no chain end deactivation takes place at each addition. To minimize cross-linking due to the attack of residual isopropenyl groups by the propagating centers, excess *s*-BuLi (10% excess relative to DIB units) was used in the activation step to ensure complete conversion of the isopropenyl moieties.

The chain extension reactions could have been carried out as true one-pot reactions analogous to the ones described above, but isolation of the G0 copolymer substrate prior to activation was preferred for practical reasons. The viscosity of arborescent polymers with long side chains ($M_n = (1-2) \times 10^4$) in semidilute solutions can be very high, which would make it necessary to add large volumes of solvent to the reaction (beyond that used to dilute the monomer) in a true one-pot process. This may cause the deactivation of some propagating centers and thus cause a decrease in branching functionality for each chain extension reaction. The decision to use the isolated copolymer was therefore motivated by the desire to

Table 4. Synthesis of Analogous G0 and G1 Polystyrenes by Successive Monomer Additions after Copolymer Isolation[a]

		$M_n/10^3$			M_w/M_n				
gen	M_n^{SC} [b]$/10^3$	SEC[c]	MALLS[d]	calc[e]	Waters[f]	PL[g]	$[\eta]$/mL g^{-1}	g′ [h]	linear/wt %
G0	2.5	40	63	72	1.50		37.0 ± 0.6	0.81	4
	5.0	88	160	137	1.47		62 ± 2	0.70	6
	10	151	410	253	1.39		104 ± 5	0.64	8
	15	222	650	490	1.26		131 ± 6	0.62	10
G1	2.5	441	760	800	1.36	1.40	34 ± 1	0.139	10
	5.0	524	1700	1700	1.22	1.27	67 ± 1	0.162	14
	10	749	3500	3100	1.17	1.19	110 ± 5	0.166	15
	20	787	7300	6000	1.13	1.07	160 ± 3	0.147	18

[a] 10% excess *s*-BuLi based on DIB content used in substrate activation; $M_n = 8300$, $M_w/M_n = 1.50$ for linear substrate; $M_n = 110\,000$, $M_w/M_n = 1.69$ for G0 substrate; 6 equiv of LiCl added after activation; d*n*/d*c* = 0.189−0.191 in THF at 632 nm used in SEC-MALLS calculations. [b] Target side chain M_n. [c] Apparent value based on linear polystyrene calibration. [d] Absolute value determined using MALLS detector. [e] Calculated M_n based on reaction stoichiometry. [f] Absolute PDI from MALLS detector with a Waters SEC column. [g] Apparent PDI from DRI detector with Polymer Laboratories ultrahigh molecular weight column and band broadening correction. [h] Hydrodynamic shrinkage factor $g' = [\eta]/[\eta]_{\text{lin}}$, where $[\eta]$ refers to an arborescent polymer and $[\eta]_{\text{lin}}$ to a linear polymer[19] of identical molecular weight.

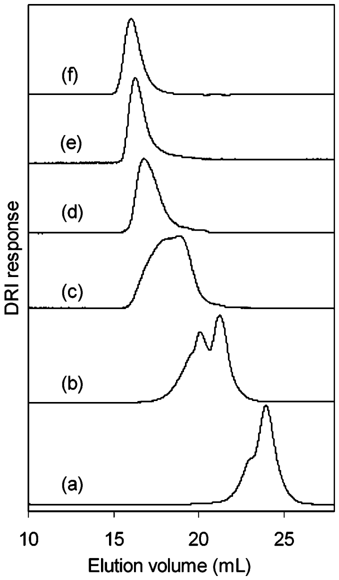


Figure 5. SEC elution curves for the synthesis of analogous G1 polystyrenes (after copolymer isolation) described in Table 4: (a) linear copolymer, (b) G0 copolymer, and fractionated G1 polymers (c) $M_n^{SC} = 2500$, (d) $M_n^{SC} = 5000$, (e) $M_n^{SC} = 10\,000$, and (f) $M_n^{SC} = 20\,000$.

obtain structurally more uniform products by minimizing chain termination in the successive monomer additions. The results obtained by both procedures are otherwise equivalent: Using the G1 polymers with $M_n = 5000$ side chains for a direct comparison, $M_w/M_n = 1.20-1.25$ for the true one-pot reactions (Table 3), while $M_w/M_n = 1.22$ with copolymer isolation (Table 4). Since residual DIB was removed in the precipitation step, all linear contaminant should arise from the excess of *s*-BuLi. This was confirmed by SEC analysis of the crude products: A narrow monomodal peak was observed for the linear contaminant without "dimeric" shoulder due to the activation of both double bonds in residual DIB (see Supporting Information).

Characterization results obtained for the two series of analogous G0 and G1 polystyrene samples with different side chain lengths ($M_n = 2500-20\,000$) are provided in Table 4, and a series of SEC elution curves illustrating the synthesis of the analogous G1 samples are provided in Figure 5. The PDI of the polymers decreases noticeably for the G1 polymers as the length of the side chains increases. A significant decrease in PDI was also noted when comparing the values obtained for the G1 polymers obtained by a single monomer addition (Table 3). It would be tempting to attribute the observed decrease in PDI to a separation artifact on the SEC column such as decreasing separation efficiency in the high molecular weight range (i.e., reaching the exclusion limit). This explanation appears inappropriate, however, because the whole MWD of the polymers synthesized elutes over the linear portion of the calibration curve for the Waters columns used. The peaks for the G0 analogous polymers, in particular, fall well within the linear range of the calibration curve and display the same trend. To confirm this trend, the measurements were repeated for the G1 samples on Polymer Laboratories PLgel 20 MIXED-A ultrahigh molecular weight columns, with a useful (linear polystyrene) separation range reaching 4×10^7, higher than that of the Waters columns (10^7). Unfortunately, the Polymer Laboratories columns suffer from considerable band broadening (ΔPDI ≈ 0.30), making it necessary to apply band broadening correction[17] to the results. The analysis results obtained for the G1 samples with both column sets are compared in Table 4. The peaks obtained on the ultrahigh-molecular-weight column are more symmetrical and the same narrowing trend exists among the G1 sample series as a function of increasing side-chain length. The PDI decrease observed is therefore not related to exceeding the separation range of the SEC columns but rather seems to be real.

A possible (albeit speculative) explanation for the origin of the PDI decrease observed for longer side-chain materials could be the differentiation of propagating site reactivity on the substrate molecules. The rate of styrene addition (side-chain extension) is expected to depend on the local concentration of styrene monomer at the propagating sites, which may be influenced by the size of the macroinitiator substrate as well as the number of initiating sites present. The monomer must diffuse to the propagating centers for chain extension to take place. Larger substrate molecules contain a larger number of initiating sites, but some of these sites are necessarily buried deeper within the substrate and less accessible than the ones on the outer portion of the substrate. Initiating sites buried within large substrate molecules also experience a less polar microenvironment, which may lead to enhanced intramolecular association and therefore a lower average reactivity. Reduced accessibility and enhanced association of the propagating centers for larger substrate molecules would both lead to self-regulation of the growth of molecules in the reaction mixture: High molecular weight substrates would tend to grow more slowly than the low molecular weight substrates due to their lower average polarity, thus causing a decrease in PDI. Reactivity differentiation (and molecular size averaging) should become more significant as the molecular weight (length) of the side chains increases because of the increasingly nonpolar microenvironment of the molecules. Furthermore, it can be seen in Table 4 that for successive monomer additions the linear contaminant content

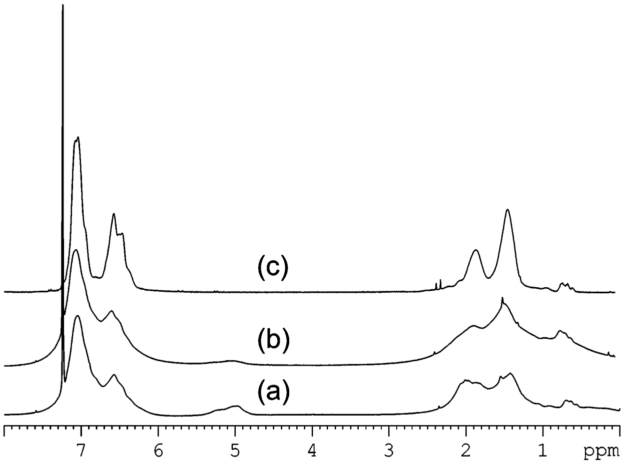


Figure 6. ^{1}H NMR spectra for (a) G0-7b styrene−DIB copolymer, (b) G0-7b substrate after activation and deactivation with methanol, and (c) G1-7b arborescent polystyrene.

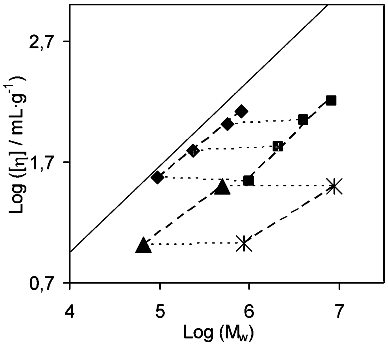


Figure 7. Dependence of intrinsic viscosity on molecular weight for arborescent and linear polymers in toluene at 25 °C: —, linear polystyrene; ◆, one-pot G0 polystyrenes (side chain $M_n = 2500$, 5000, 10 000, and 15 000); ■, one-pot G1 polystyrenes (side chain M_n = 2500, 5000, 10 000, and 20 000); ▲, stepwise G0 polystyrenes (side chain $M_n = 5000$ and 30 000); * stepwise G1 polystyrenes (side chain $M_n = 5000$ and 30 000).

of the samples (due to residual *s*-BuLi) increases with the molecular weight of the side chains. This observation is in agreement with the lower reactivity postulated for propagating sites within the polyfunctional macroinitiator than for those at the end of linear chains. Differences in propagating center reactivity imply that the dimensions of the individual side chains may be less uniform in the grafting-from procedure proposed than in typical anionic polymerization reactions. A broad MWD for the side chains does not preclude the attainment of a narrow MWD for the whole graft polymer sample, however, since the MWD of the side chains is being averaged f_w chains at a time (f_w = branching functionality). The dimensions of the side chains ($M_n = 2500{-}20\,000$) cannot be determined directly but rather represent the target molecular weights calculated on the basis of the reaction stoichiometry.

Polymer Characterization. When comparing the absolute number-average molecular weights (M_n) as determined by MALLS analysis for the linear, G0, and G1 polymers in Table 4 (fourth column), it is clear that the molecular weight increases in an approximately geometric fashion for successive generations. The absolute molecular weights are up to 9.2 times larger than the apparent (polystyrene-equivalent) molecular weights determined by SEC analysis using a linear polystyrene standards calibration curve (third column), in analogy to arborescent polystyrenes synthesized previously.[2,3] Theoretical M_n values are also provided in Table 4 (fifth column). These were calculated on the basis of the molecular weight of the substrates and the amount of monomer added to the reaction, corrected for the linear polymer formed. The molecular weights measured by MALLS are somewhat higher than the calculated values, presumably due to cross-linking reactions.

^{1}H NMR spectra are compared in Figure 6 for a G0 styrene−DIB copolymer, an activated and subsequently deactivated G0 styrene−DIB copolymer, and a G1 polystyrene sample. Aromatic proton resonances are observed in the 6.0−7.3 ppm range, the methylene protons of isopropenyl moieties give a broad peak around 4.8−5.3 ppm, and aliphatic proton resonances are in the 1.0−2.3 ppm range. The area of the peak at 4.8−5.3 ppm in curve (a) is greatly reduced in curve (b) but nonzero because only 95% of the isopropenyl moieties on the backbone were activated (as for the reactions with substoichiometric activation). The spectrum of Figure 6b confirms the presence of residual isopropenyl groups in the substrate, responsible for the PDI increase and gel formation. The aliphatic signals in curve (b) are broader than before activation, possibly due to reduced backbone mobility resulting from intra- and intermolecular cross-linking reactions, as the PDI of the copolymer increased from 1.68 to 1.80 upon treatment with *s*-BuLi. The NMR spectrum of the final G1 polymer sample (with a side-chain target M_n = 5000) essentially corresponds to that of pure polystyrene because of the large weight fraction of that component in the molecules.

The intrinsic viscosity values [η] in toluene determined for the analogous arborescent polystyrene samples synthesized by successive monomer additions are provided in Table 4, together with the errors corresponding to the 95% confidence limits for the measurements.[18] The scaling behavior of [η] for the one-pot G0 (diamonds) and G1 (squares) arborescent polystyrenes is compared in Figure 7 with that of linear polystyrenes[19] (solid line) as well as arborescent polystyrenes obtained by the stepwise grafting-onto method for generations G0 (triangles) and G1 (stars).[15]

The intrinsic viscosity of the polymers, obtained by extrapolation of the reduced viscosity (η_{sp}/c) to zero concentration (c), is inversely proportional to the so-called hydrodynamic density (V_h/M) of the macromolecules at infinite dilution according to the Einstein equation:

$$[\eta] = \lim_{c\to 0} \frac{\eta_{sp}}{c} = \frac{2.5 N_A V_h}{M} \tag{1}$$

The Mark−Houwink−Sakurada (MHS) equation $[\eta] = KM_v{}^a$ likewise describes the exponential dependence of intrinsic viscosity on the viscosity-average molecular weight M_v (for low PDI polymers $M_w \approx M_v \approx M$ in the equations). The slope of the solid lines in Figure 7 corresponds to the scaling exponent a in the MHS equation. If the variation in [η] is considered at constant generation number as a function of increasing side chain molecular weight for the G0 and G1 one-pot arborescent polymers, the trends are similar for both sample series (G0: a = 0.59; G1: a = 0.73) and for the linear polymers (a = 0.71).[19] However, the trends are very different if the variation in [η] is considered at constant side-chain molecular weight as a function of generation number. While the number of data points available for such a comparison is very limited (two points in each series, corresponding to the G0 and G1 samples), the lines obtained (shown as dotted lines in Figure 7) are essentially flat for both the one-pot and the stepwise arborescent polymers. This means that the hydrodynamic density of the molecules remains constant (or independent of branching functionality) at constant side-chain molecular weight for arborescent polymers synthesized by both methods. Alternately, it can be stated that the hydrodynamic density of arborescent polymers is dominated by the size of the side chains grafted and not by the generation number (branching functionality) of the molecules, in analogy to star-branched polymers.[20] The hydrodynamic density of arborescent polymers synthesized by the one-pot method is lower than for the stepwise samples, however, since their intrinsic viscosity is higher at comparable molecular weight. For example, $[\eta]$ for the one-pot samples with $M_w = 2500$ side chains is comparable to that of stepwise samples with $M_w = 30\,000$ side chains. Since the branching density used is similar for the one-pot and the stepwise samples, the higher $[\eta]$ values observed for the one-pot samples could either be due to intermolecular cross-linking reactions increasing the asymmetry of the molecules or be linked to the presumed nonuniform dimensions of the side chains within the molecules.

Nonetheless, all the one-pot samples have intrinsic viscosities lower than linear polymers of comparable molecular weights, as shown by the hydrodynamic shrinkage factors g' reported in Table 4. The G0 and G1 sample series display relatively minor variations in the contraction factors ($g' = 0.69 \pm 0.09$ and 0.15 ± 0.01 for the G0 and G1 series, respectively), but the G1 samples are clearly more compact than their G0 analogues. For the G1 sample with $M_w = 2500$ side chains $g' = 0.139$, corresponding to a 7.2-fold decrease in intrinsic viscosity relative to the linear polymer.

Conclusions

A one-pot procedure based on the copolymerization of styrene and DIB was developed for the synthesis of arborescent G0 and G1 polystyrenes. A semibatch monomer addition protocol produced the best results in terms of polydispersity index attained and reproducibility. Analogous series of branched polymers with varying side chain lengths were obtained by successive monomer additions. The intrinsic viscosity of the arborescent polystyrenes synthesized is higher than for samples obtained by the stepwise approach, but still up to ca. 7 times lower than for linear samples. The one-pot grafting-from scheme may be easily extended to the synthesis of arborescent copolymers by substituting styrene with a different monomer in the last chain growth reaction. This approach will be discussed in a subsequent paper.

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Supporting Information Available: Experimental details and discussion of linear styrene−DIB copolymer synthesis. This material is available free of charge via the Internet at http://pubs.acs.org.

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