A Novel Synthetic Path to Arborescent Graft Polystyrenes

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ABSTRACT: A method for the preparation of arborescent polystyrenes based on acetyl coupling sites is described. The acetyl functionalities are randomly introduced on the grafting substrate by reacting polystyrene with acetyl chloride in the presence of anhydrous $AlCl_3$ in nitrobenzene. Anionic polymerization of styrene with *sec*-butyllithium yields polystyryllithium serving as side chains; coupling of the side chains with the acetylated substrate generates the graft polymers. Direct coupling of polystyryllithium with acetylated polystyrene suffers from a low grafting yield (∼65% for a linear substrate), due to deactivation of the macroanions by side reactions. End-capping of polystyryllithium with a few isoprene or 2-vinylpyridine units, along with the addition of LiCl, increases the grafting yield to >95%. Repetition of acetylation and anionic grafting cycles leads to generations of arborescent polymers with a low polydispersity index ($M_w/M_n = 1.07-1.09$). The polymers are characterized by a very compact structure and by a branching functionality and molecular weight increasing geometrically for successive generations. Tailor-designed arborescent architectures are attainable by this "graft-on-graft" procedure, by controlling the acetylation level and the molecular weight of the side chains used for each grafting reaction.

Introduction

Polymers with a dendritic architecture have attracted much attention due to their intriguing structure, properties, and expanding applications. Dendritic polymers encompass a wide range of compounds with a cascade-branched structure including dendrimers, hyperbranched polymers, and arborescent graft polymers. Numerous synthetic methods have been suggested for preparing these materials.[1−5]

Using "living" polymerization and successive grafting reactions of polymeric building blocks, arborescent graft polymers[6] (or dendrigraft polymers[7]) have been synthesized to minimize some of the problems encountered in dendrimer and hyperbranched polymer syntheses. The increases in branching functionality and molecular weight attained per generation are much higher than for dendrimer syntheses. Arborescent polymers with over 10^3 branches and a molecular weight reaching 10^8 can be prepared in 2−4 reaction cycles. The structure of arborescent polymers is well-defined in terms of branching functionality, branch length, and molecular weight distribution (MWD, typically $M_w/M_n \approx 1.1$). Graft polymers with a dendritic structure analogous to hyperbranched systems have also been obtained recently in a one-pot reaction of oligomeric polystyryllithium with 4-(chlorodimethylsilyl)styrene.[8]

The arborescent polymer synthesis requires the introduction of suitable coupling sites on the substrate. Chloromethyl functionalities have been used to prepare arborescent polystyrenes[6] as well as copolymers based on an arborescent polystyrene core grafted with polyisoprene[9] or poly(2-vinylpyridine)[10] side chains. The introduction of chloromethyl groups involves electrophilic substitution with chloromethyl methyl ether, a potent carcinogen.[11] While the reaction of polystyryllithium with chloromethyl sites is efficient (up to 96% coupling achieved), it is not very practical due to safety and environmental concerns. It would be preferable to rely on a more innocuous reagent for functionalization of the substrate. The new grafting reaction should nevertheless proceed in high yield, to facilitate purification steps such as fractionation of the products.

Carbonyl functionalities are well-known for their addition reaction with nucleophilic compounds such as Grignard reagents and other reactive anions. Acetylation of polystyrene was considered as a path for the introduction of coupling sites for macroanions in this study. The acetylation of polystyrene is conveniently carried out with acetyl chloride in the presence of a Lewis acid (e.g., $AlCl_3$) in nitrobenzene.[12] We are now reporting on the synthesis of arborescent graft polystyrenes using the acetyl functionality, based on the living anionic polymerization technique and successive grafting reactions of polymeric building blocks.

Experimental Section

Solvent and Reagent Purification. Tetrahydrofuran (THF; Caledon, reagent grade) was distilled from sodium benzophenone ketyl under nitrogen. Toluene (BDH, ACS reagent) was distilled from oligostyryllithium under nitrogen. The dry solvents were introduced directly from the stills into the polymerization reactor or ampule preparation manifolds through poly(tetrafluoroethylene) (PTFE) tubing. Styrene (Aldrich, 99%), α-methylstyrene (α-MS, Aldrich, 99%), isoprene (IP, Aldrich, 99%), and 2-vinylpyridine (2VP, Aldrich, 97%) were distilled after stirring over CaH_2 overnight. 1,1-Diphenylethylene (DPE, Aldrich, 97%) was purified by adding enough *n*-butyllithium solution (Aldrich, 2.5 M in hexanes) to obtain the deep red 1,1-diphenylhexyllithium coloration and reduced pressure distillation. The monomers were stored under nitrogen at −20 °C until a second purification step immediately before use. *sec*-Butyllithium (Aldrich, 1.3 M in cyclohexane) was used as received; the exact activity of the solution was determined by the method of Lipton et al.[13] Acetyl chloride (Aldrich, 99+%) was distilled under nitrogen. Nitrobenzene (Aldrich, 99%) was distilled under reduced pressure. All other reagents were used as received. All reagent ampules used in the polymerization and grafting procedures were prepared by high-vacuum techniques and then filled with dry nitrogen. The ampules, equipped with PTFE stopcocks and

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ground glass joints, could be mounted directly on the polymerization reactor.[14]

Styrene Polymerization. Styrene (44 mL, 0.384 mol) was further purified immediately before polymerization with phenylmagnesium chloride and polymerized in a glass reactor, first in toluene (300 mL) at room temperature with *sec*-butyllithium (8.0 mmol, for a calculated $M_n = 5000$).[14] After 15 min the reactor was cooled to −78 °C, and dry THF (200 mL) was added slowly to increase the rate of polymerization. The reaction was terminated with degassed methanol after 15 min.

Acetylation of Polystyrene. A 7.5 g sample of polystyrene (72 mequiv of styrene units) was dried under vacuum and dissolved in 100 mL of nitrobenzene. A catalyst solution was prepared by dissolving 3.15 g (24 mmol) of anhydrous $AlCl_3$ (Aldrich, 99.99%) in 10 mL of nitrobenzene, followed by 1.85 mL (26 mmol) of acetyl chloride. The catalyst was added dropwise to the polymer solution over 30 min, and the reaction was allowed to proceed further for 30 min. The acetylated polymer was precipitated in acidified methanol (1.5 L + 50 mL of concentrated HCl). The polymer was further purified by reprecipitation in acidified methanol from THF, redissolution in chloroform, extraction with a H_2O/HCl mixture (50/50 v/v) and distilled water, and precipitation in methanol. The same procedure was used to acetylate branched polystyrenes serving as substrates for the synthesis of higher generation arborescent polymers.

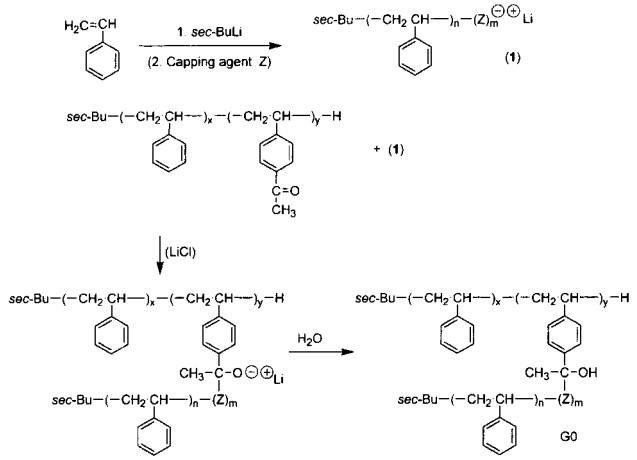
Grafting Reaction. Arborescent polystyrenes were prepared by coupling living polystyryl anions with the acetylated polystyrene substrates. For a typical reaction, ampules containing purified styrene monomer (15 g diluted in 75 mL of THF), 2VP (if used, 1 g in 10 mL of THF), and the acetylated polystyrene substrate (1.4 g in 30 mL of THF, 3.6 mequiv of acetyl groups) were first prepared. Styrene was polymerized in 300 mL of THF at −78 °C for 10 min, using 3 mmol of *sec*-butyllithium in the presence of 15 mmol of LiCl. The 2VP solution was then added slowly to give a color change from orange to dark red. A sample of the 2VP-capped polystyryl anions was removed from the reactor and terminated with degassed methanol for characterization of the side chains. The living polymer was slowly titrated with the acetylated polystyrene solution over 30 min to a light red color. Stirring was continued for 30 min, and residual living polymer chains were deactivated with degassed water. The product was recovered by precipitation in methanol and subjected to fractionation with a toluene−methanol mixture to remove nongrafted chains.

Polymer Characterization. Size exclusion chromatography (SEC) analysis was performed for the substrates before and after acetylation, the side chains, the raw grafting products, and the fractionated graft polymers. The system used consists of a Waters 510 HPLC pump equipped with a Jordi 500 mm DVB linear mixed-bed column and a Waters 410 differential refractive index (DRI) detector. The polymers were analyzed in THF at a flow rate of 1 mL/min. Polystyrene equivalent molecular weights and polydispersity indices (M_w/M_n) were determined for the samples using a linear polystyrene standards calibration curve.

The absolute weight-average molecular weight (M_w) and M_w/M_n of many samples were determined from SEC-MALLS (multiangle laser light scattering) measurements using a Wyatt Dawn DSP-F instrument operating at 632.8 nm. The effect of the second virial coefficient was not considered in the molecular weight calculations, which may result in slightly (<5%) underestimated molecular weight values.[6] The SEC-MALLS system consists of a Waters 590 programmable HPLC pump coupled with Waters Ultrastyragel columns (10^4, 10^5, and 10^6 Å pore sizes) using THF at a flow rate of 1 mL/min. Polymer concentration measurements in the eluent are accomplished with a Waters 2410 DRI detector. Samples based on generation G2 substrates could not be analyzed by SEC-MALLS because the samples were retained on the column. Their absolute M_w was determined using static light scattering measurements on a Brookhaven BI-200 SM light scattering goniometer equipped with a Lexel 2 W argon ion laser operating at 514.5 nm.[14] The M_w was determined by Zimm extrapolation to zero angle and concentration for a series of measurements for eight solutions in toluene at angles ranging from 30° to 150°.

^{1}H NMR spectroscopy served to determine the acetylation level of the grafting substrates. The NMR spectra were recorded in $CDCl_3$ on a Bruker AM-250 spectrometer.

Scheme 1. Grafting Reaction on Linear Acetylated Polystyrene To Produce a Comb (G0) Polymer; in Some Cases a Capping Agent Z Was Used



Results and Discussion

The coupling reaction between polystyryllithium and acetylated polystyrene is described in Scheme 1. It involves nucleophilic addition of either polystyryllithium or the capped macroanion (capping agent Z = DPE, α-MS, IP, or 2VP) on the carbonyl group. The synthesis comprises three steps: The substrate is randomly acetylated to introduce coupling sites; the polymerization of styrene with *sec*-butyllithium generates living polystyryllithium, which may be end-capped to modify its reactivity; and titration of the living polymer with the acetylated substrate produces the graft polymer. Specific aspects of each step will now be discussed in more detail.

Linear Polystyrene and Acetylation Procedure. The linear polymer obtained in a toluene/THF mixture has the expected molecular weight ($M_w = 5100$) and a narrow MWD ($M_w/M_n = 1.07$). Acetylation of this polymer yielded a substrate with a substitution level of 25 mol % as determined by ^{1}H NMR spectroscopy. SEC analysis of the acetylated polymer yielded an apparent (polystyrene equivalent) $M_w = 5700$ and $M_w/M_n = 1.07$. While the SEC analysis results before and after acetylation cannot be compared directly, the low polydispersity index values obtained for both samples suggest that the acetylation reaction proceeds without cross-linking or chain cleavage reactions.

Acetylation of polystyrene was performed with acetyl chloride in the presence of anhydrous $AlCl_3$ according to the Perrier procedure[12] by adding a mixture of the catalyst and acetyl chloride to the polymer solution in nitrobenzene. Compared to chloromethylation with chloromethyl methyl ether (CMME), the acetylation reaction presents some important advantages. Acetyl chloride is much more innocuous than CMME. It is also easier to control the functionalization level in acetylation than in chloromethylation: A large excess of CMME must be used in the chloromethylation reaction,[6,15] leading to the deactivation of variable amounts of catalyst, depending on the purity of the reagent used.

Table 1. Direct Grafting of Polystyryllithium on Acetylated Polystyrene: Effect of Temperature and Solvent Composition[a]

temp/ °C	solvent	PS side chains		graft polymer		grafting yield (%)[e]
		M_w[d]	M_w/M_n[d]	M_w[d]	M_w/M_n[d]	
−30	THF/tol[b]	4700	1.08	28 900	1.09	64
0	THF/tol[b]	5400	1.07	32 400	1.10	65
25	THF/tol[b]	5700	1.10	34 600	1.12	64
−30	THF[c]	5200	1.11	31 000	1.12	65
0	THF[c]	5800	1.09	35 500	1.10	65
25	THF[c]	5300	1.10	32 100	1.11	64

[a] All reactions with linear polystyrene substrate (M_w = 5100, M_w/M_n = 1.07, acetylation level = 25 mol %). [b] Mixed solvent composition is 1:2 v/v THF/toluene. [c] Styrene monomer added as a 20% solution in THF. [d] Determined using SEC analysis based on a linear polystyrene standards calibration curve. [e] Fraction of side chains generated attached to the substrate.

In contrast, the acetylation level is controlled by nearly stoichiometric amounts of $AlCl_3$ and acetyl chloride. Furthermore, chloromethylation is prone to cross-linking reactions, while acetylation is not.

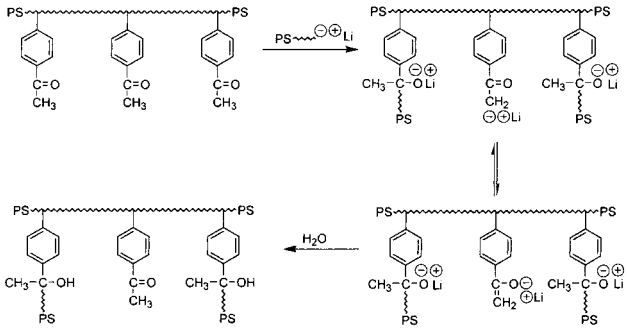
The acetylation level is easily determined by ^{1}H NMR spectroscopy. The introduction of the acetyl group causes two new resonances at δ = 2.55 ppm (acetyl group) and δ = 7.65 ppm (aromatic protons ortho to the acetyl group) in the spectrum. Variation of the acetylation level provides control over the branching density on the backbone and thus over the structural rigidity of the polymers.[16] In this study, the acetylation level was maintained at 20−30 mol % for all generations, to generate 10−15 grafting sites per $M_w \approx 5000$ polystyrene side chain.

Grafting of Polystyryllithium. To maximize the grafting yield, defined as the fraction of living chains generated that becomes attached to the substrate, the conditions were first optimized for the reaction of the macroanions with linear acetylated polystyrene. The variables investigated are the composition of the reaction medium, the grafting temperature, the use of capping agents, and the addition of LiCl as a stabilizer for the macroanions. For each test reaction, $M_w \approx 5000$ polystyrene side chains were grafted onto a randomly acetylated M_w = 5100 linear polystyrene substrate with a substitution level of 25 mol %.

To investigate the influence of solvent composition and temperature on the grafting yield, the reactions were performed either in a mixed toluene/THF (1:2 v/v) system or in pure THF. When the grafting reaction was performed in toluene/THF, styrene was first polymerized in toluene at 25 °C for 10 min. After cooling the reactor to −78 °C, THF was added to increase the polymerization rate. For grafting in pure THF, the polymerization was performed at −78 °C, and the monomer was slowly added as a 20% solution in THF. In each case, grafting was attempted at −30, 0, and 25 °C. Table 1 summarizes the results obtained for the coupling reactions.

Grafting proceeds with 64−65% yield in all cases. It is clear that neither the solvent composition nor the temperature has a significant influence on the reaction. SEC analysis of the crude products indicates that the nongrafted material has a M_w identical with the side chain sample removed prior to grafting and hence results simply from deactivation of the propagating centers. This is very different from the situation encountered in grafting polystyryllithium onto chloromethyl functionalities, where dimerization of polystyryllithium is an important side reaction. Dimerization arises from metal−halogen exchange of the living chains with the chloromethylated substrate to give a chlorine-terminated chain, followed by coupling with another polystyryllithium molecule.[6,17]

Scheme 2. Grafting and Competing Enolate Formation Reaction



Since the polystyryl anion is highly reactive, protonation of the anion is likely to be responsible for the "monomeric" termination mechanism observed. The carbonyl group not only provides a site for nucleophilic addition (the grafting reaction) but also acidifies the methyl hydrogens of the acetyl functionality. When polystyryllithium attacks the acetyl functionality, enolate formation and termination of the macroanion may compete with coupling (Scheme 2). This side reaction ultimately leads to the regeneration of a fraction of the acetyl functionalities during sample workup. Experimental evidence in support of enolate formation was obtained in a model reaction of the linear acetylated substrate (M_w = 5100, 25 mol % acetylation) with polystyryllithium of relatively low molecular weight (M_w = 1500). The graft polymer, obtained in 64% yield, contained 2.8 mol % residual acetyl functionalities after purification by fractionation. The residual acetyl group content calculated based on the backbone and side chain M_w, assuming that 64% (7.7) of the 12 coupling sites on the substrate are used up in the reaction, is also 2.8 mol %. This suggests that enolate formation is the only side reaction competing with coupling. Similar acidic hydrogen abstraction reactions have been observed, for example, in the sulfoalkylation reaction of polystyryllithium with 1,3-propane sultone, where abstraction by polystyryllithium of an acidic proton α to the sulfur atom decreases the functionalization yield.[18]

Polystyryllithium Reactivity Attenuation by End-Capping. Conversion of the highly reactive polystyryl anion to a less reactive entity by end-capping is a widely used approach to avoid side reactions. For example, in preparing styrene−methyl methacrylate block copolymers, attack on the carbonyl group of the methacrylate monomer can be avoided by "capping" polystyryllithium with DPE prior to addition of the second monomer.[19] The same capping agent was also useful to avoid side reactions in the preparation of telechelic polystyrenes[20] and in coupling polystyryllithium with chloromethyl functionalities.[6]

Considering the many applications of DPE reported in the literature, the usefulness of capping with DPE and other monomers in acetyl group coupling was also investigated. The grafting yields obtained using different capping agents for polystyryllithium are summarized in Table 2. Since DPE does not homopolymerize, using ca. 1.2 equiv of DPE with respect to the active chains in a reaction ensures that all chains are capped.

Table 2. Optimization of Grafting Yield by End-Capping[a]

temp/ °C	capping agent	capped side chains		graft polymer		grafting yield (%)[f]
		M_w[e]	M_w/M_n[e]	M_w[e]	M_w/M_n[e]	
0	DPE[b]	5100	1.08	20 900	1.15	40
0	α-MS[c]	4900	1.11	22 700	1.13	47
0	α-MS[d]	5200	1.12	24 500	1.12	47
0	IP[c]	5400	1.08	34 000	1.09	68
0	IP[d]	5100	1.07	31 800	1.10	68
−30	IP[c]	5300	1.10	36 000	1.11	74
0	2VP[c]	5100	1.09	33 200	1.10	71
−30	2VP[c]	5600	1.07	40 100	1.09	79

[a] All reactions in THF with linear polystyrene substrate (M_w = 5100, M_w/M_n = 1.07, acetylation level = 25 mol %); styrene monomer added as a 20% THF solution. [b] 1.2 equiv of 1,1-diphenylethylene (DPE) used for the capping reaction. [c] Side chains capped with 3 equiv of capping agents, α-methylstyrene (α-MS), isoprene (IP), or 2-vinylpyridine (2VP). [d] Side chains capped with 10 equiv of capping agents, α-MS, or IP. [e] Apparent values determined using SEC analysis based on a linear polystyrene standards calibration curve. [f] Fraction of side chains generated attached to the substrate.

DPE capping does not increase the grafting yield but actually decreases it from ∼65% to 40% at 0 °C. This can be explained by the strongly hindered structure of the DPE-capped macroanion, facilitating enolate formation (Scheme 2) at the expense of nucleophilic addition.

Another capping agent investigated is α-methylstyrene (α-MS). In this case, polystyryllithium was reacted with either 3 or 10 equiv of α-MS prior to grafting. It is found that the number of capping units used has no influence on the reaction. The grafting yield (∼47%) is higher than for DPE capping but still lower than for noncapped polystyryllithium, again confirming the importance of steric factors in the grafting reaction.

On the basis of the results obtained for DPE and α-MS, capping agents with reduced steric crowding such as isoprene were considered to increase the grafting yield. This reagent has been used to improve the coupling efficiency to chlorosilanes in star-branched polymer syntheses.[21,22] Capping of the chains with either 3 or 10 equiv of isoprene led to identical grafting yields at 0 °C, indicating that 3 equiv suffices to cap all chains. Capping with isoprene increases the yield from ∼65% to 68% and 74% for reactions at 0 and −30 °C, respectively (Table 2). The increased yield at lower temperatures presumably reflects a reduced tendency for enolate formation, while a sufficiently high reactivity is maintained in the coupling reaction. These results show that not only steric effects but also the reactivity of the macroanion play important roles in the grafting reaction.

Another capping agent, 2-vinylpyridine (2VP), was employed to yield macroanions with a lower reactivity than isoprene, while maintaining steric factors comparable to nonmodified polystyryllithium. In the anionic copolymerization of isoprene and 2VP it is known that cross-propagation from polyisoprenyllithium to 2VP is easy, but poly(2-vinylpyridinyl)lithium is too unreactive to attack isoprene. Capping with 2VP led to further improvements in grafting yield from ∼65% to 71% and 79% for reactions at 0 and −30 °C, respectively. Considering the higher yields obtained, isoprene and 2VP were further investigated as capping agents for the grafting reaction of polystyryllithium with acetylated polystyrene.

Polystyryllithium Reactivity Attenuation with LiCl. It is known that the addition of a common ion salt to an anionic polymerization reaction leads to a reduced propagation rate, due to shifting of the ion pair vs free anion equilibrium in favor of ion pairs.[23] Ion pairs have a much lower reactivity and a higher stability compared to the free anions. This approach to avoid side reactions is well-documented for the anionic polymerization of acrylates and methacrylates.[24,25] The usefulness of salt addition was investigated by using 5 equiv of LiCl in the grafting reactions, after capping the chains with either isoprene or 2VP. Table 3 summarizes the results obtained under these conditions.

Table 3. Optimization of Grafting Yield in the Presence of LiCl[a]

temp/ °C	capping agent	side chains		graft polymer		grafting yield (%)[d]
		M_w[c]	M_w/M_n[c]	M_w[c]	M_w/M_n[c]	
−30	none	5200	1.07	31 800	1.11	65
0	none	5000	1.09	29 700	1.10	64
−30	IP[b]	4900	1.08	38 400	1.08	86
0	IP[b]	4700	1.10	39 700	1.09	93
25	IP[b]	5700	1.09	49 200	1.08	96
−30	2VP[b]	5500	1.08	45 100	1.08	92
0	2VP[b]	5200	1.07	45 500	1.07	97
25	2VP[b]	5400	1.09	46 200	1.09	95

[a] All reactions in THF with linear polystyrene substrate (M_w = 5100, M_w/M_n = 1.07, acetylation level = 25 mol %); 5 equiv of LiCl added; styrene monomer added as a 20% THF solution. [b] Side chains capped with 3 equiv of isoprene (IP) or 2-vinylpyridine (2VP). [c] Determined using SEC analysis based on a linear polystyrene standards calibration curve. [d] Fraction of side chains generated attached to the substrate.

For the direct grafting reaction of polystyryllithium onto acetylated polystyrene the addition of LiCl has no detectable effect, the grafting yield remaining at ∼65%. For chains capped with isoprene or 2VP, in contrast, the grafting yield is strongly increased, reaching over 95% at 0−25 °C. The complete elimination of side reactions under the optimized conditions is verified by slightly overtitrating the living polymer solution to a colorless end point with the acetylated polystyrene. The peak corresponding to nongrafted side chains in SEC analysis completely disappears, indicating the absence of deactivation reactions. In practice, undertitration of the macroanions solution, to leave a small amount (3−5%) of nongrafted side chains, is considered preferable to produce graft polymers with a better-defined structure.

In summary, capping of polystyryllithium with a few isoprene or 2VP units, along with the addition of LiCl, can be used to increase the coupling yield of polystyryllithium and linear acetylated polystyrene to over 95%.

Arborescent Graft Polystyrenes. Using the conditions optimized for the synthesis of comb-branched (G0) polystyrene, two series of arborescent polystyrenes with either short ($M_w \approx 5000$, PS5) or long ($M_w \approx 30\,000$, PS30) side chains grafted onto acetylated polystyrene substrates of different generations were prepared, to examine the influence on the grafting reaction of the side chain molecular weight and of the substrate generation used. Characterization data for the polymers obtained are summarized in Table 4. The substrates G0PS, G1PS, and G2PS were prepared by repetition of acetylation−grafting−fractionation cycles using a side chain $M_w \approx 5000$ for each generation. Arborescent polymers based on either isoprene- or 2VP-capping were initially investigated as grafting substrates. It was found that polymers synthesized from polystyryllithium capped with 3 equiv of isoprene suffer from minor (∼5%) side chain cleavage during the acetylation process, as

Table 4. Characteristics of Arborescent Polystyrenes of Successive Generations[a]

	side chains[c]			graft polymer				
sample[b]	M_w[d]	M_w/M_n[d]	grafting yield (%)[e]	M_w[d]	M_w/M_n[d]	M_w[f]	f_w[g]	coupling efficiency (%)[h]
PS-PS5	4400	1.09	95	5.3×10^4	1.08	3.3×10^4	11	92
G0PS-PS5	4500	1.07	89	4.3×10^5	1.08	1.3×10^5	84	84
G1PS-PS5	5000	1.08	84	3.9×10^6	1.09	4.5×10^5	690	70
G2PS-PS5	5500	1.09	75	2.5×10^7			3800	57
PS-PS30	28500	1.09	87	3.2×10^5	1.08	1.9×10^5	11	92
G0PS-PS30	28700	1.07	75	2.1×10^6	1.07	4.7×10^5	71	71
G1PS-PS30	27800	1.06	55	1.1×10^7	1.09	7.1×10^5	380	39
G2PS-PS30	28500	1.08	43	6.1×10^7			2000	30

[a] All reactions in THF at 0 °C with 5 equiv of LiCl added; styrene monomer added as a 20% THF solution. [b] Acetylation level of the substrates for PS: 25 mol %, G0PS: 22 mol %; G1PS: 27 mol %; G2PS: 20 mol %. [c] Side chains capped with 3 equiv of 2VP. [d] Absolute values determined by SEC-MALLS or laser light scattering measurements. [e] Fraction of side chains generated attached to the substrate. [f] Apparent values determined using SEC analysis based on a linear polystyrene standards calibration curve; samples G2PS−PS5 and G2PS−PS30 not eluted from the column in SEC analysis. [g] Number of branches added in the last grafting reaction. [h] Fraction of available coupling sites on the substrate consumed.

determined by SEC analysis of the acetylated polymers. For chains capped with 15 equiv of isoprene, 21% side chain cleavage is observed. Polyisoprene containing 3,4-units is known to undergo cationic cyclization and chain scission reactions in the presence of Lewis acids.[26] It has been postulated that chain scission reactions are most probable at the junction between 1,4- and 3,4-units. Since the capping reaction was carried out in THF, a mixed chain microstructure (with equal proportions of 1,2-, 1,4-, and 3,4-isoprene units) is expected. The cationic scission mechanism would explain why more chain cleavage is observed when the number of isoprene units used to cap the chains is increased. Addition of HCl to the polymer before acetylation, to induce cyclohydrochlorination of the isoprene units,[27] did not eliminate chain cleavage or lead to cross-linking reactions. On the basis of the cleavage reactions observed, the polymers prepared from isoprene-capped chains are deemed unsuitable as substrates for the preparation of higher generation graft polymers. In contrast, no chain cleavage is detected during the acetylation of polymers prepared using 2VP capping. Consequently, grafting of LiCl-stabilized macroanions capped with 3 equiv of 2VP units onto acetylated polystyrene substrates in THF at 0 °C was selected as a standard procedure for the preparation of arborescent polystyrenes.

The nomenclature used for the samples identifies the generation number of the substrate as well as the molecular weight of the side chains used in the reaction. For example, G1PS-PS5 refers to a G1 polystyrene substrate grafted with $M_w \approx 5000$ side chains in the last reaction, while G1PS-PS30 refers to the same substrate grafted with $M_w \approx 30\,000$ side chains. It should be noticed that sample PS-PS5 becomes substrate G0PS after acetylation, G0PS-PS5 becomes the G1PS substrate, and so on.

The results in Table 4 demonstrate that as the branching functionality (generation) of the substrate or the molecular weight of the grafted side chains is increased, the grafting yield decreases. This effect is most pronounced for G1 and G2 substrates grafted with $M_w \approx 30\,000$ side chains. An important factor contributing to the deactivation of the living anions in the preparation of higher generation polymers may be their reaction with residual protic impurities introduced with the substrate polymer solution: It is more difficult to purify the higher generation substrates after acetylation. To reach the end point (complete discoloration of the living anions) in the grafting procedure, an excess of higher generation substrates must be used. This method, while ensuring full consumption of the anions (and a maximized grafting yield), leads to the introduction of a larger amount of protic impurities in the reaction. Dependence of the grafting yield upon the length of the polystyrene grafts is also observed: Comparison of the grafting yield for substrates of the same generation shows that it is always lower for the PS30 than for the PS5 series samples. This effect is most noticeable with the G2 substrates. The concentration of living ends decreases when the molecular weight of the side chains increases, making the reaction more susceptible to deactivation by impurities.

The coupling efficiency, defined as the fraction of coupling sites on the substrate consumed in the reaction, follows similar trends to the grafting yield. The decrease observed for higher generation substrates is attributed to increased congestion leading to reduced accessibility of the coupling sites. Two distinct "phases" were identified within arborescent polystyrenes in a fluorescence quenching investigation of the molecules.[28] The more rigid inner portion of the molecule was found to be less accessible to quencher species than the more flexible outer portion. The fraction of less accessible material was also found to increase for higher generation polymers.

There is experimental evidence that the grafting reaction on G1 and G2 acetylated substrates becomes diffusion-limited. The amount of linear and G0 acetylated polymers required in the titration of the living polymers is approximately as expected from the stoichiometry of the reaction. For substrates G1 and G2, however, a 30−50% excess of substrate is required to deactivate all the living ends. This, again, is consistent with surface overcrowding effects sterically hindering the diffusion of the living chain ends to the acetyl sites. Steric effects were also reported as a limiting factor in the preparation of dendrimers.

A grafting reaction was attempted to maximize the coupling efficiency by using an excess of macroanions allowed to react with the substrate for a long time. The reaction of a G1 substrate with $M_w \approx 30\,000$ side chains capped with 2VP was used for this purpose. In contrast to the general method which consists of titrating the polystyryllithium solution with a solution of the acetylated substrate over approximately 1 h, the reaction was allowed to proceed for 4 h with a 30 mol % excess of side chains. The red coloration of the solution persisted over that period. Residual anions were then terminated with degassed water. As expected, the fraction of side

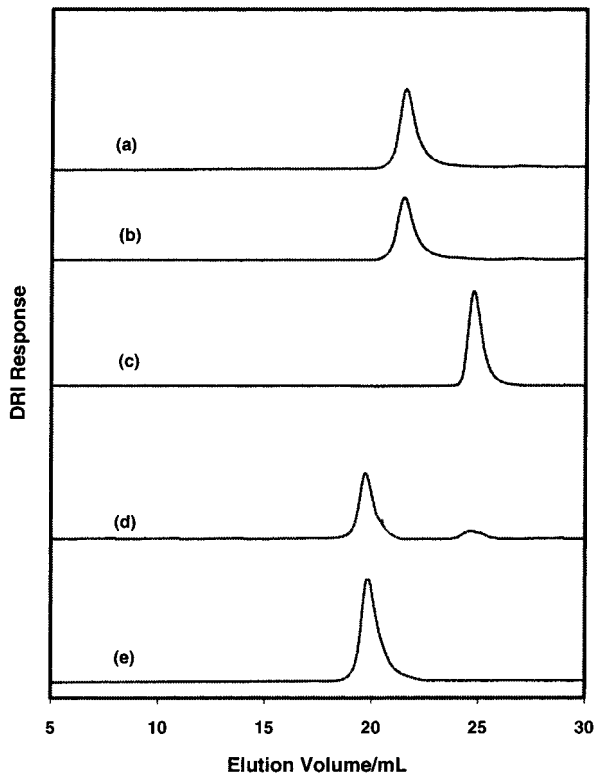


Figure 1. Preparation of sample G0PS-PS5: SEC traces for (a) G0PS sample before acetylation, (b) acetylated G0PS substrate, (c) 2VP-capped polystyryllithium side chains, (d) crude product from the grafting reaction, and (e) fractionated graft polymer.

chains grafted (grafting yield) decreased from ~55% to ~35%. However, the absolute M_w of the graft polymer was identical for both reactions, indicating that the coupling efficiency is only limited by the extent of steric congestion within the substrates. Grafting of shorter side chains, grafting onto a less congested substrate, or decreasing the acetylation level should, therefore, increase the coupling efficiency.

Sample Characterization. SEC characterization was performed for the substrates before and after acetylation, the side chains, the crude grafting products, and the fractionated polymers. Figure 1 provides SEC curves illustrating the preparation of sample G0PS-PS5 with traces for the substrate before and after acetylation, the side chains (M_w = 4500), the crude grafting product, and the fractionated polymer. Comparison of curves a and b shows that the MWD of the substrate is unaffected by the acetylation reaction, the polydispersity remaining constant (M_w/M_n = 1.08). The polystyrene side chains have a narrow MWD (M_w/M_n = 1.07 for curve c). Generally two peaks, corresponding to the graft polymer and to nongrafted side chains, can be observed in the SEC trace for the crude product (curve d). The high molecular weight (leftmost) peak corresponds to the graft polymer. The peak on right has the same molecular weight as the side chain sample removed before the grafting reaction (curve c). It corresponds to linear chains deactivated by residual impurities present in the acetylated polymer solution or the capping agent solution. Comparison of curves b and d demonstrates that no excess acetylated substrate is present in the product. This is a consequence of the colorimetric titration procedure used, allowing precise control over the stoichiometry of the reaction. Curve e confirms complete removal of the nongrafted side chains by fractionation.

The grafting yield can be calculated from the SEC trace for the raw product, by comparing the peak area for the graft polymer to the total area of both peaks. For sample G0PS-PS5 (Figure 1, curve d), for example, a grafting yield of 89% was obtained. The grafting yields reported in Tables 1−4 were obtained in this manner, except for samples derived from the G2PS core. Samples G2PS-PS5 and G2PS-PS30 were not eluted from the SEC column, and only the nongrafted side chains were detected. It is still possible to calculate the grafting yield in this case by comparing the response obtained for the nongrafted material in the crude product to the response for a polystyrene standard of known concentration. For sample G2PS-PS5, for example, the peak area for the nongrafted chains in the crude product (in arbitrary units) was 20 200. The peak area for a linear sample injected at the same concentration was 80 600 units. The peak area ratio for the measurements is 20 200/80 600 = 0.25, corresponding to 25% nongrafted side chains or 75% graft polymer. The grafting yield was confirmed gravimetrically on the basis of the mass of purified graft polymer recovered after fractionation. The grafting yields obtained gravimetrically for samples G2PS-PS5 and G2PS-PS30 are 74% and 41%, respectively, in good agreement with the SEC values presented in Table 4.

The absolute M_w of the graft polymers, determined either by on-line (SEC-MALLS) or batch light scattering measurements, is reported in Table 4, along with the apparent values determined by SEC analysis using a DRI detector. It is evident that the apparent M_w values are strongly underestimated, especially for higher generations. This is due to the very compact (hard-sphere) structure of arborescent polymers, as confirmed by static and dynamic light scattering,[16] and by viscosity measurements.[29] The polydispersity index remains low (M_w/M_n = 1.07−1.09) over successive generations of the graft polymers.

The branching functionality (f_w) of the arborescent polymers, defined as the number of chains added in the last grafting reaction, was calculated from the equation

$$f_w = \frac{M_w(G) - M_w(G-1)}{M_w^{br}} \qquad (1)$$

where $M_w(G)$, $M_w(G-1)$, and M_w^{br} are the absolute weight-average molecular weight of graft polymers of generation G, of the preceding generation, and of the side chains, respectively. The f_w values listed in Table 4 range from 11 to 3800 for the PS5 series and from 11 to 2000 for the PS30 series. Both sample series display a roughly geometrical increase in molecular weight and f_w with generation number.

Conclusions

The results presented show that the acetyl functionality is suitable as a grafting site for the synthesis of arborescent polystyrenes. Acetyl functionalities can be easily introduced on polystyrene using acetyl chloride in the presence of $AlCl_3$ in nitrobenzene. This process eliminates the need for chloromethyl methyl ether, a highly toxic and carcinogenic reagent previously used to introduce chloromethyl grafting sites. Optimization of the reaction conditions made high grafting yields (>95%) possible. Repetition of the acetylation and

anionic grafting sequences led to well-defined arborescent polymers ($M_w/M_n = 1.07-1.09$) with a very compact structure and a degree of branching and molecular weight increasing geometrically for successive generations.

Capping with isoprene or 2-vinylpyridine provides a successful path for the synthesis of arborescent polystyrenes. While these materials are useful as model branched polymers, there is also strong interest in producing arborescent polymers with a wider range of chemical and physical properties. This can be achieved by introducing side chains with a different chemical composition in the grafting process. For this reason, the synthesis of arborescent copolymers containing polyisoprene and poly(2-vinylpyridine) side chains, based on the acetyl functionality, will be examined subsequently.

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