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Uniform Highly Branched Polymers by Anionic Grafting: Arborescent Graft Polymers†

Mario Gauthier and Martin Möller*

Institut für Makromolekulare Chemie, Albert-Ludwigs-Universität Freiburg, Stefan-Meier-Strasse 31, D-7800 Freiburg, Germany

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ABSTRACT: A grafting technique leading to macromolecules apparently analogous to previously reported cascade molecules is described. Well-defined polystyrenes ($M_w/M_n \approx 1.1$–1.3) with degrees of branching and molecular weights increasing geometrically for each generation are obtained in a new "graft on graft" procedure involving chloromethylation–anionic grafting sequences. Optimization of the reaction conditions made high grafting yields (>95%) possible, with a negligible amount of side reactions taking place. Molecular weights of up to (3–4) × 10^6 were obtained after three chloromethylation and grafting cycles, the polydispersity of the materials increasing slightly for successive generations. Characterization results with the help of gel permeation chromatography–light scattering, viscometry, and osmometry show that the polymers prepared have a very compact structure in solution, and yet a low density (0.2 g/mL), indicative of a "hollow" structure.

Introduction

The synthesis and characterization of starburst[1-5] and arborol[6,7] cascade-type molecules have recently in part coincided with a considerable amount of theoretical and practical interest[8-10] in macromolecules with a hollow spherical topology. The unique structure of these materials represents a challenge in terms of the ability to control accurately the structural characteristics of synthetic polymers, which make them relevant to macromolecular engineering techniques. One limitation encountered in the synthesis of cascade structures is that, because the molecules used as building blocks have a low molecular weight, the rate of increase in molecular weight per generation is relatively low. Many synthetic steps are therefore necessary to produce high molecular weight materials. The cascade growth process also has the disadvantage of being intrinsically very sensitive to incomplete or side reactions leading to structure imperfections.[1,5,10] To avoid this problem, large excesses of reagents are sometimes necessary, which can make them difficult, although necessary, to eliminate prior to subsequent reaction steps.

In order to avoid these problems, the possibility of obtaining synthetic high polymers with spherical symmetry using a different approach has been considered. The new method is based on the production of graft polymers with monomer units able to serve again as grafting sites for the next generation. This "graft on graft" procedure results in polymers with a treelike structure (Figure 1), in analogy to cascade-type molecules. In this case, however, the grafted branches are distributed randomly along the chains serving as backbone, rather than strictly at their ends.

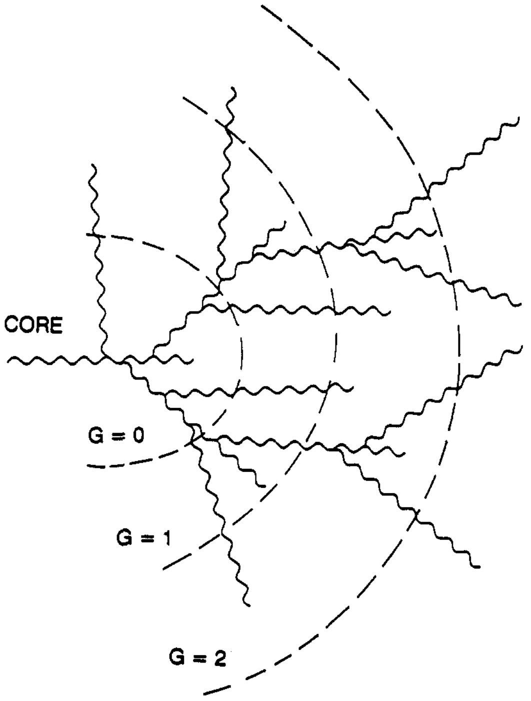

Figure 1. Simplified representation of the expansion of arborescent graft polymers as a result of successive grafting reactions. The dotted lines and numbers show the diffuse layer growth process for up to generation $G = 2$.

Following the nomenclature suggested by Tomalia et al. for cascade-type molecules,[1] the central polymer unit of Figure 1 may be considered as a "core". Grafting side chains of comparable molecular weight on this linear core merely result in a classical comb-branched structure, designated generation zero ($G = 0$ on Figure 1). Repeating this grafting process, however, yields a much more crowded structure (generation 1), which, based on steric restrictions, should be forced to expand toward the outside, assuming presumably a globular or spheroidal structure. This globular structure should become further perfected as a result of repeating the grafting process (second generation).

Considering the essentially treelike or arborescent structure of these novel materials and the grafting technique used to obtain them, we coined the term *arborescent graft polymers* to describe them.

If the molecular weight per branch (M_b) and the branching functionality (f) remain constant for each generation (G), arborescent graft polymers are obtained with molecular weights ideally increasing geometrically according to the equation

$$M = M_b + M_b f + M_b f^2 + \ldots = \sum_{x=0}^{G+1} M_b f^x \qquad (1)$$

With a sufficiently high branching functionality (f = 10–

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* To whom correspondence should be sent. Present address: Department of Chemical Technology, University of Twente, P.O. Box 217, NL-7500 AE Enschede, The Netherlands.

† Dedicated to Prof. Dr. W. Burchard on the occasion of his 60th birthday.

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20), and if the grafting sites are distributed randomly throughout the molecules, most of the material added in a grafting reaction will be on the outer branches of the preceding generation. The molecules will therefore expand as a result of somewhat diffuse added layers for each generation, represented by the dotted boundaries on Figure 1.

Even though the structure of arborescent graft polymers is not as strictly controlled as in the case of the starburst or arborol compounds, a number of advantages of this technique become obvious. Because the building blocks are polymers rather than small molecules, the molecular weight of the products grows much more rapidly; fewer reaction steps are necessary to prepare high polymers. Random distribution of the grafting sites makes the growth process less sensitive to side reactions than cascade growth, all molecules being affected by side reactions to the same extent and in a similar manner, on the average. As will be shown later, however, due care was still taken to minimize the occurrence of side reactions in the grafting process, in order to optimize grafting efficiency. Consequently, no particular purification procedure was necessary for the products, except for fractionation to separate a minor fraction of ungrafted chains from the graft polymers. The polymerization and grafting reactions are carried out sequentially in a single reactor. This one-pot approach further simplifies the synthetic aspects of this procedure. One distinct advantage of the arborescent graft polymers is the possibility to control easily the structure of the macromolecules obtained merely by varying either the branching density or the molecular weight of the branches. Well-defined macromolecules with a wide range of molecular weights and topologies varying from spheres to ellipsoidal or rodlike shapes of controllable rigidity can thus be synthesized.

It is the aim of this paper to show that the synthesis of arborescent graft polymers using the graft on graft approach is indeed possible and practical. As an illustrative example, the synthesis of styrene polymers with a branching functionality $f \approx 15$ and a branch molecular weight of ca. 5000 is described for up to the second arborescent graft polymer generation ($G = 2$). Preliminary results for the characterization of these materials are then discussed.

Synthetic Strategy

The anionic polymerization technique is known to be one of the best methods to generate macromolecules with a narrow molecular weight distribution.[11] It therefore seemed natural to make use of this approach for the preparation of the present model polymers. Living polymers, in particular, are highly reactive species, well-suited to the preparation of graft polymers, where the grafted chains can be either of the same or of a different composition as the backbone.[12] All-styrene graft polymers have been prepared on a number of occasions[13-16] and were based on a coupling reaction involving chloromethylated polystyrene and the living polystyryl anions. It was recognized that the coupling efficiency was fairly low, most of the time less than 50-60%.[13-15] While some attempts were made to optimize coupling efficiency, there are also a number of contradictory reports on this subject. For example, essentially 100% coupling was reported when potassium, rather than lithium, was the counterion for the living polymer in the preparation of four-arm star polymers from 1,2,4,5-tetrachloromethylbenzene.[17] Lower yields (80%) were, however, found by another group[16] in the preparation of comb polymers from chloromethylated polystyrene under similar conditions. The nature of the side reactions limiting the coupling efficiency was also studied[18] and essentially involves a metal-halogen exchange reaction competing with the coupling reaction.

In light of the literature published on this topic, it became obvious that it was necessary to develop reaction conditions such that the grafting efficiency is optimized but for which the results obtained are consistent for various runs. Polystyryl anions are known to be highly reactive entities, which have sometimes caused problems, for example, in the preparation of styrene-methyl methacrylate[19] or styrene-vinylpyridine[20] block copolymers. The highly reactive carbanions could, apart from adding to the vinyl bond of the second component, also attack the pyridine ring or the carbonyl bond of the reactive monomer. This led to branching of the products. One way suggested[19,21] to avoid this problem was to reduce the reactivity of the polystyryl anion by "capping" the living polymer with a single 1,1-diphenylethylene unit prior to adding the second monomer. Nucleophilic attack reactions leading to branching could thus be avoided. More recently, the same reagent also proved to be useful in the preparation of terminally functionalized polystyrenes,[22,23] which would otherwise also have suffered from side reactions.

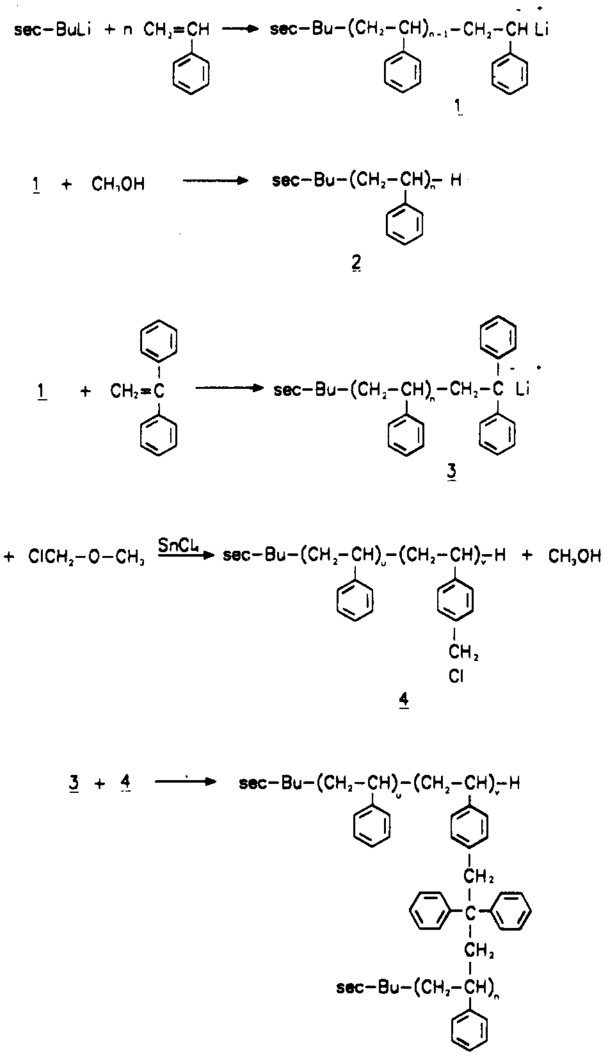
It therefore seemed that the same approach might prove useful in optimizing the grafting reaction in the preparation of arborescent graft polymers. The synthetic scheme selected would therefore include the polymerization of styrene in benzene at room temperature with *sec*-butyllithium, in order to obtain living polymers (ca. 5000 g/mol) with a narrow distribution. The coupling reaction being apparently more efficient when carried out in the presence of tetrahydrofuran (THF) than in benzene alone,[16] the capping agent 1,1-diphenylethylene would be introduced in the reaction as a solution in THF. The living polymer solution could then be slowly titrated to near discoloration with a solution of chloromethylated polystyrene. Grafting techniques involving a chloromethylated polystyrene solution being added to the living polymer, as well as the reverse procedure, have been reported in the literature.[13-16] However, the first method was preferred here, since it seemed to be easier from an experimental point of view and to provide maximum control over the titration procedure. The different steps of the synthetic scheme used can be summarized by the equations in Scheme I.

Another variable of interest in the grafting procedure is the temperature at which the coupling reaction is carried out. Because of wide variations in experimental conditions used in the literature, the effect of this particular variable on the grafting efficiency was not clear. It was therefore to be investigated in a systematic manner under otherwise identical reaction conditions.

In view of slight unsystematic variations in the coupling efficiency, it later became necessary to examine the effect of an additional variable on the preparation of the graft polymers, namely, that of the drying technique used for chloromethylated polystyrene. While in the first attempts, the polymer was simply dried under high vacuum overnight; azeotropic removal of residual water with THF proved to be superior for drying the chloromethylated backbone polymer.

Finally, a last aspect that had to be considered was the need to keep the molecular weight distribution as narrow as possible for each generation. This becomes particularly important in the preparation of model macromolecules such as the arborescent graft polymers, because broadening of the distribution also gets transferred to the following generations. Chloromethylation of polystyrene is known

Scheme I



to suffer from a few limitations,[24-26] one of which is the tendency to form cross-links in the course of the reaction. This would lead, in this case, to the formation of dimers, trimers, and multimers and consequently cause a broadening of the molecular weight distribution. Reaction conditions therefore also had to be selected for the chloromethylation, which would cause minimal, if any, increase in polydispersity.

All the synthetic parameters of interest being optimized, systematic repetitions of the chloromethylation–grafting procedure should therefore yield macromolecules with the desired architecture, namely, the arborescent graft polymers.

Experimental Section

Synthesis. Styrene monomer (Aldrich, 99%) was purified by two distillations over CaH_2 at reduced pressure; 1,1-diphenylethylene (DPE; Aldrich, 97%) was also distilled at reduced pressure after adding a solution of *n*-butyllithium to obtain the deep red 1,1-diphenylhexyllithium anion coloration. Benzene was dried by refluxing with potassium–benzophenone ketyl under inert atmosphere and introduced directly from the distillation still into the polymerization reactor. Tetrahydrofuran (THF) used in the preparation of ampules and for azeotropic drying was dried by the same technique. *sec*-Butyllithium was obtained from Aldrich as a 1.4 M solution in cyclohexane; the exact activity of the initiator was determined by the Gilman double-titration procedure.[27] Carbon tetrachloride (Merck, p.a.) was dried over P_2O_5. Chloromethyl methyl ether was prepared according to a known method.[28] All other reagents were used as obtained from the suppliers. Reagent ampules with PTFE stopcocks, used in the polymerization and grafting procedures, were prepared with the help of high-vacuum techniques and then filled with purified nitrogen.

Table I
Optimization of Reaction Conditions in the Preparation of Comb-Branched ($G = 0$) Graft Polymers

sample	DPE used	temp, °C	polymer drying	grafting, %
S05-0-1	no	25	HV[a]	50
S05-0-2	yes	25	HV	80
S05-0-3	yes	50	HV	79
S05-0-4	yes	0	HV	86
S05-0-5	yes	−30	HV	80
S05-0-6	yes	−30	azeotrope[b]	96

[a] Chloromethylated polymer dried overnight under high vacuum. [b] Polymer dried by azeotropic distillation of residual water with THF.

Core Polymer. A solution of styrene monomer (20 g, 0.192 mol) in benzene (20 mL) was degassed and further purified, prior to polymerization, by stirring with dibutylmagnesium (0.9 M solution in heptane, 5 mL; Alfa), followed by slow recondensation to an ampule. Polymerization of the monomer was initiated with *sec*-butyllithium (4 mmol) in dry benzene (500 mL) under inert atmosphere. After 4 h the polymerization reaction was stopped by injecting 1 mL of degassed methanol in the reactor. Polystyrene with ca. 15 grafting sites/chain, serving as core, was obtained by the chloromethylation of the anionically prepared polystyrene (M_n = 5200 and M_w/M_n = 1.07). Typical reaction conditions were 10 g of polymer in 500 mL of dry carbon tetrachloride, 60–80 mL of chloromethyl methyl ether, and 1 mL of stannic chloride. The reaction time for ca. 30 mol % chloromethylation (determined by ^1H NMR spectroscopy) was 48–72 h at room temperature.

Comb-Branched Polymers. In addition to the monomer ampule mentioned above, an ampule containing THF alone or with added 1,1-diphenylethylene (DPE), as well as a chloromethylated polystyrene ampule, was also prepared. When used as a reactivity modifier for the polystyryl anions, DPE (6 mmol, i.e., 50 mol % excess based on the amount of initiator used) was loaded in the ampule and dried by azeotropic distillations with two 30-mL portions of still-dried THF, before redissolution in 350 mL of dry THF. Chloromethylated polystyrene (6 mequiv, based on the chloromethylation level) was loaded in an ampule and dried overnight under high vacuum. For azeotropic drying, two 30-mL portions of dry THF were used to dissolve the polymer and then evaporated, before redissolving the polymer in 30 mL of dry THF again.

The preparation of the comb-branched graft polymers involved polymerization of a styrene monomer (20 g) in dry benzene as described above as the first step. Dry tetrahydrofuran (350 mL), with or without added DPE, was then added from the ampule to the polymerization reactor. The living polymer solution was then slowly titrated, over 30 min, to a pale orange (without DPE) or red (with DPE) with the solution of chloromethylated polystyrene. Stirring was continued for 30 min, after which time the intensity of the colored carbanion solution had further decreased. The remaining living polymer chains were finally deactivated by injecting 0.5–1 mL of degassed methanol in the reactor. After workup, the ungrafted chains were separated from the graft polymer by fractionation in a toluene–methanol mixture. Successful fractionation was confirmed by a comparison of GPC diagrams for the fractionated and unfractionated samples.

The reaction conditions were varied in a systematic manner in order to optimize the yield of the grafting process. The investigated variables were the presence of 1,1-diphenylethylene as a reactivity modifier, the variation of the temperature used for the grafting reaction, and azeotropic drying of the chloromethylated polymer. The conditions used for the preparation of generation 0 (comb-branched) polymer samples S05-0-1 through S05-0-6 are summarized in Table I.

Arborescent Graft Polymers. Generation 1 and 2 polymers were prepared by using the same general techniques used for generation 0 graft polymers. Chloromethylation of fractionated generation 0 and 1 graft polymers to 30 mol % as described for the core polymer yielded precursors for arborescent graft polymer generations 1 and 2, respectively. The formation of a small fraction of microgel-like particles was observed in the preparation of the second generation (S05-2-1) sample. These could be removed by fractionation or centrifugation of the products.

Characterization

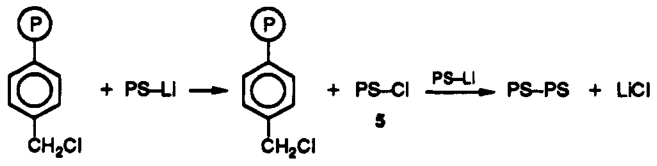
Because the compounds prepared have a highly branched structure, it was necessary to rely on absolute methods for molecular weight determinations, mainly in the form of gel permeation chromatography–light scattering (GPC–LS) measurements. This technique has the advantage of yielding the real molecular weight distribution for branched polymers, in contrast to the normal GPC procedure using the elution volume dependence of linear standard polymers for calibration. The system consisted of a Pharmacia P-500 nonpulsating pump coupled with Waters μ-Styragel columns (10^4-, 10^5-, and 10^6-Å pore sizes). Polymer concentration measurements in the eluent were accomplished with a Waters R403 differential refractometer. A Milton-Roy (Chromatix) KMX-6 low-angle laser light scattering (LALLS) detector, used in series with the dn/dc detector, allowed continued molecular weight evaluation of the eluted polymer fractions. Calibration of the LALLS unit was accomplished by comparing the measured Rayleigh ratio for toluene to the theoretically expected value. Toluene also served as eluent, the flow rate being 0.5 mL/min and the operating pressure about 30 bar. Sample concentration was 10 mg/mL, and the injection volume, 100 μL. The refractive index increment of the branched polymers, verified for the S05-2-1 sample with a Brice–Phoenix refractometer was, as expected, $dn/dc = 0.110$ at 633 nm, identical with that of linear polystyrene.[29] The effect of the second virial coefficient was not considered in the molecular weight calculations ($A_2 = 0$), which may result in slightly underestimated molecular weight values, with the error expected to be 5% or less.

Vapor pressure osmosis measurements (for the polystyrene core) were carried out on a Hewlett-Packard 115 molecular weight apparatus. The instrument was calibrated with bibenzyl in chloroform at 30 °C. Membrane osmosis measurements (samples S05-0-2 and S05-1-1) in THF were made on a Hewlett-Packard 502 high-speed membrane osmometer equipped with a regenerated cellulose membrane.

The intrinsic viscosities of different polymer samples were determined in toluene with the help of a Schott AVST automated Ubbelohde-type capillary viscometer. The stock solutions (200 mg/50 mL) were filtered twice with a 0.5-μm PTFE filter prior to the measurements.

Results and Discussion

Synthesis. The effects of different reaction conditions used for the preparation of the graft polymers could be quantified from the GPC curves (dn/dc) detector) obtained for the unfractionated products (Figure 2). Up to three peaks could be identified in the GPC diagrams, the leftmost peak (at $V_e = 29$ mL) corresponding to the graft polymer. The second peak at ca. 10 000 g/mol ($V_e = 31.5$ mL) results from dimerization of the living polymer chains following a halogen–metal exchange reaction with the chloromethylated polymer.[18]



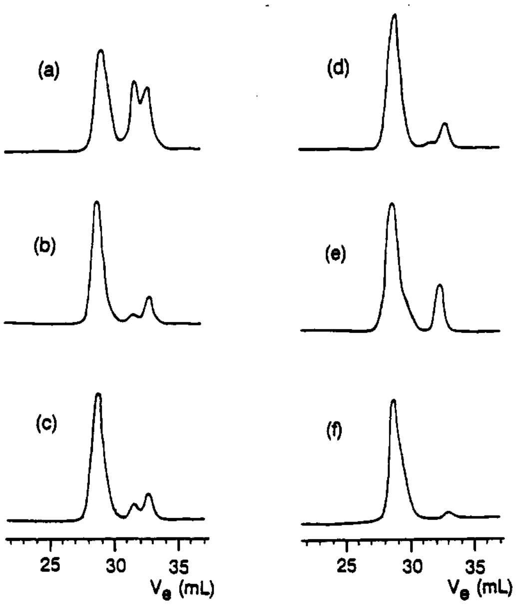


Figure 2. GPC diagrams of generation 0 (comb-branched) graft polymers: (a) S05-0-1, (b) S05-0-2, (c) S05-0-3, (d) S05-0-4, (e) S05-0-5, (f) S05-0-6. The scales indicate the corresponding elution volumes (V_e).

The last peak at ca. 5000 g/mol ($V_e = 33$ mL) could either correspond to an unreacted intermediate (5) above or simply to polymer anions deactivated by residual water present in the chloromethylated polymer.

A comparison of the peak areas under the graft polymer and those attributed to the side reactions gives a grafting efficiency of 50% for sample S05-0-1 (diagram a, Figure 2), a value comparable to those reported for the present reaction under similar conditions,[16] a large amount of dimer being present. Comparison with diagram b of Figure 2, however, shows that, even at room temperature, the use of 1,1-diphenylethylene as a chain capper markedly reduced the occurrence of side reactions, the grafting efficiency being increased to 80%. The effects of varying the temperature at which the grafting reaction is carried out is illustrated in diagrams b–e of Figure 2 for reaction temperatures of +25, +50, 0, and −30 °C, respectively. The graft polymer obtained at 50 °C seems to be comparable to that obtained at 25 °C, the grafting efficiency being identical (79%), within error limits. At 0 °C, however, the amount of side reactions leading to linear dimer formation becomes minimal, to disappear completely at −30 °C (diagram e, Figure 2).

It should be noted that the slight asymmetry of the graft polymer peak of sample S05-0-5 (diagram e, Figure 2) resulted from titrating the living polymer solution too quickly rather than from side reactions. The coupling reaction being controlled by definite reaction kinetics, it is necessary to titrate the polystyryl carbanions very slowly in order to avoid overtitrating. Otherwise, it results in the exhaustion of the carbanion supply; a portion of the graft polymers are thus left with unreacted chloromethyl groups and hence fewer grafted side chains. This causes the shoulder on the low molecular weight side of the graft polymer, observed in diagram e of Figure 2. The absence of dimers in sample S05-0-5, and the somewhat variable intensity of the 5000 g/mol peak (cf. diagrams d and e, Figure 2), suggested that this peak might result from residual water in the chloromethylated polymer rather than from side reactions. This was confirmed by drying the polymer with an azeotropic technique (i.e., first dissolving the polymer in dry THF and then evaporating the solvent, before redissolution in fresh THF) rather than

Table II
Characterization of Arborescent Graft Polymers and Precursors

sample	M_n(GPC) × 10^3	M_w(GPC) × 10^3	M_n(os) × 10^3	[η], mL/g	[η](lin), mL/g
core	5.2	5.6	5.0	6.3	
S05-0-2	111	126	120	15.2	35.7
S05-1-1	750	840	2000	11.7	130.0
S05-2-1	3400	4400		13.0	527.0

with high vacuum alone (diagram f, Figure 2). The small amount (4–5%) of ungrafted chains left in the reaction is considered to be necessary, in order to avoid overtitrating the polystyryl anions.

In summary, the best reaction conditions for the grafting reaction are represented by sample S05-0-6 and involve azeotropic drying of the chloromethylated polymer, capping of the polystyryl anions with 1,1-diphenylethylene, and slow titration of the living polymer at −30 °C.

As previously mentioned, a critical point in obtaining arborescent graft polymers that retain a narrow molecular weight distribution for each successive generation is that no cross-linking takes place in the chloromethylation reaction. Chloromethylation under normal conditions with chloromethyl methyl ether and $SnCl_4$ is known to lead to cross-linking.[24] This problem was avoided here by working under very dilute conditions (2% w/v) and using a large excess of chloromethyl methyl ether (8.2–11 mol/mol of styrene) but mostly by keeping the amount of Lewis acid ($SnCl_4$) to a minimum (0.1 mL/g of polymer). This is actually the main factor controlling the chloromethylation kinetics, since the "catalyst" gets destroyed by methanol produced in the reaction. The fact that the molecular weight distribution was unaffected by chloromethylation was verified by GPC, in the form of unchanged polydispersity indices.

There are, however, some indications that the grafting reaction may become diffusion-controlled in the case of the second generation sample. The amount of chloromethylated polymer used for the titrations in preparing generation 0 and 1 polymers was about as expected from the equivalent weight determined by NMR. For sample S05-2-1, however, even the whole amount of chloromethylated polystyrene (50 mol % excess with respect to amount of initiator) contained in the titration ampule did not suffice to deactivate all living polymer chains. The molecular weight obtained is also significantly lower than expected (1 × 10^7 g/mol), taking the molecular weights and chloromethylation levels obtained for each generation into account. This may be indicative of steric effects (surface overcrowding) hindering the diffusion of the living polymer chains to the chloromethylated sites, resulting in a reduced grafting efficiency. This is presumably analogous to surface overcrowding effects also reported as a limiting factor in the preparation of cascade-type molecules.[2,3,8,10]

Characterization. An examination of the molecular weights determined by gel permeation chromatography–light scattering (GPC–LS) for different arborescent graft polymer generations (Table II) shows that the width of the molecular weight distributions remains relatively narrow ($M_w/M_n \approx 1.1$–1.3) for each generation. This shows that the idea of applying the graft on graft procedure to the preparation of polymers with an arborescent structure is justified and successful. The polymers obtained have a molecular weight increasing in a geometric fashion for each generation, the polydispersity of the products increasing only slightly in the process.

A number of advantages may be noticed when comparing the arborescent graft polymers to the more classical starburst- or arborol-type polymers. The most striking difference involves the much faster increase in molecular weight per generation for grafted polymers. This is a result not only of higher molecular weight per repeat unit (ca. 5000) but also of a higher branching functionality of the units ($f \approx 10$–15/chain). While molecular weights in the millions range are obtained for second generation arborescent graft polymers, the corresponding starburst- or arborol-type polymers have a molecular weight of 10^4 or less[1-7]. The graft polymers are therefore obtained in high yields (>90–95%) in a one-pot reaction, and the only purification step required is a fractionation of the ungrafted side chains. One limitation of the arborescent graft polymers, however, is that the structure of the polymers obtained is not as strictly controlled as in the case of the starburst or arborol polymers, because of the statistical nature of the graft site distribution along the chains.

Table III
Molecular Dimensions of Arborescent Graft Polymers and Comparison with Linear Polymers, As Calculated from [η] Values in Table II

sample	R_h(br), nm	R_h(lin), nm	V_h(lin/br)	density, g/mL
S05-0-2	6.7	7.7	1.5	0.16
S05-1-1	11.6	21.0	5.9	0.21
S05-2-1	20.9	62.3	26.5	0.19

Osmosis measurements provide confirmation, to a certain extent, for the molecular weights measured by GPC–LS, although the error limits can be relatively large for high molecular weights (ca. 50% for S05-1-1).

The very compact structure of the arborescent graft polymers is confirmed by the viscosity measurements (Table II). From the second generation on, the intrinsic viscosity remains relatively insensitive to the molecular weight (or degree of branching), in analogy to results previously reported for styrene star-shaped polymers with a variable number of branches.[30,31] The measured intrinsic viscosity is also much smaller than that calculated for linear polymers of corresponding molecular weights using the Mark–Houwink equation with $k = 7.5 \times 10^{-3}$ mL/g and $a = 0.75$ for toluene solutions at 25 °C.[32]

Further confirmation of the very compact structure of the arborescent branched polymers can be found in the hydrodynamic volumes V_h calculated for the arborescent graft polymers by using the Stokes–Einstein equation

$$V_h = M_w[\eta]/2.5N \qquad (2)$$

from the measured molecular weight M_w, intrinsic viscosity [η], and Avogadro's number N. The calculated hydrodynamic radii (R_h) for the various samples are compared, in Table III, with those calculated for linear polymers of comparable molecular weights with the same equation using the corresponding intrinsic viscosity values. This results in hydrodynamic volumes up to 26 times smaller for the branched molecules than for the linear polymers, expressed in Table III as the ratio of the two, V_h(lin/br). This is again indicative of extensive shrinkage of the synthesized polymers as a result of branching.

Finally, the calculated densities of arborescent graft polymers, also given in Table III, have an approximately constant value of 0.2 g/mL for generations 0–2. This is virtually identical with the density calculated for starburst polymers from published results.[1,4] Consequently, the arborescent graft polymers must have a relatively hollow structure, in analogy to the cascade molecules previously prepared.

Conclusions

The results presented here have shown that the graft on graft approach is a practical technique for the preparation of arborescent grafted polymers. High molecular weights ($>10^6$) were obtained after three grafting reactions, the polydispersity remaining narrow ($M_w/M_n \approx 1.1-1.3$) for each generation. The grafted polymers were shown to have molecular dimensions in solution that were much more compact than those for corresponding linear polystyrenes. The relative insensitivity of intrinsic viscosity to molecular weight increase for each generation, as well as their small hydrodynamic radii compared to linear polymers shows that arborescent graft polymers have a very compact structure.

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