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Polystyrene with Dendritic Branching by Convergent Living Anionic Polymerization

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ABSTRACT: The synthesis of two types of polystyrene with dendritic branching was achieved through the development of a novel method that combines living anionic polymerization with a convergent process in a one-pot reaction. The method is based on the slow addition of a reactant such as 4-(chlorodimethylsilyl)styrene (CDMSS), which contains a polymerizable vinyl group and a moiety capable of undergoing quantitative S_N2 reaction, to a solution of living polystyryl anions. The sequence of reactions results in star-shaped polymers with the initial chains forming the arms and the residue from the CDMSS forming a hyperbranched core. Different amounts of styrene monomer were added along with the CDMSS in order to increase the molecular weight between branch points. The molecular weights and polydispersities of the dendritic polystyrenes were characterized by GPC coupled with MALLS. The molecular weights of dendritic polystyrenes without added comonomer corresponded to dendritic growth of the core of 3.1−3.4 average generations with polydispersities less than 1.5. The observed narrow molecular weight distributions were interpreted using a kinetic model that relates increased steric hindrance around the reactive site to the reaction rate constants of different size dendritic polymers formed during the reaction. Adding a comonomer along with the coupling agent allowed for the synthesis of high molecular weight dendritic polystyrene (up to $M_n > 600\,000$ g/mol) and generational growth approaching an average of six generations. Intrinsic viscosities of all dendritic polystyrenes produced were found to be much lower than that of linear polystyrene. Thermal analysis of the dendritic polystyrenes showed that T_g versus molecular weight corresponded well to that of linear polystyrene normalized to the number of end groups, being slightly higher due to the effect of branching.

Introduction

Since the first reported syntheses of dendrimers,[1−3] there has been a significant research effort dedicated to finding new and simpler approaches for the formation of such highly branched macromolecules. The development of a convergent method,[4−6] in contrast to the divergent methods previously utilized, yielded a technique with control over the number of reactive sites and the focal point functionality. These two general synthetic methods of dendrimer synthesis have been used to prepare numerous examples[7,8] of compositionally different materials with unique globular shapes.

Approximations to the regular structure of dendrimers have been accomplished through the synthesis of hyperbranched polymers. Hyperbranched polymers are similar to dendrimers, but with a less regular structure resulting from a less controlled synthetic procedure. Reaction of AB_n monomers where the A and B groups can react with each other yet are mutually exclusive in their reaction with themselves is required, and this has led to condensation reactions as the predominant polymerization method. Hyperbranched polymers of a variety of compositions have been synthesized, including polyphenylenes,[9,10] polyesters,[11−14] polysiloxysilanes,[15] and others, many of which have been recently reviewed.[7,16] The molecular weight distributions of such hyperbranched polymerizations were originally examined by Flory,[17,18] who demonstrated that as conversion proceeds the polydispersity tends toward infinity. These imperfectly branched polymers are attractive because their syntheses can be accomplished in one-pot, eliminating the need for multiple reaction and purification steps typical of true dendrimer syntheses, but the large polydispersities in molecular weight and structure do not necessarily lead to the same properties as those of dendrimers.

Although condensation reactions have been the predominant synthetic method, innovative approaches using controlled cationic,[19] nitroxide-mediated free radical,[20] atom transfer radical,[21] and more recently group transfer[22] polymerization methods have extended the types of hyperbranched materials that can be formed to those from vinyl-containing monomers. The reported experimentally determined polydispersities of these materials are large (except for ref 20) and have been examined theoretically by Müller.[23]

Other techniques have also been used to prepare polymers with dendritic branching. Comb-burst dendrimers[24] and arborescent graft polymers[25−28] have been prepared by successive grafting reactions of polymer chains, resulting in dendritic materials with polymeric spacers between branch points. Low-polydispersity materials are ultimately produced, although the techniques require isolation and purification via fractionation at each step to remove unreacted polymer.

The one-pot synthesis of vinyl polymers with dendritic branching and low polydispersity in molecular weight and structure is the goal of the research reported here. To accomplish this, we have devised a convergent synthetic method[29] that takes advantage of the benefits of living anionic polymerization. The method involves living anionic polymerization to yield macromonomers in-situ that can be subsequently added to other growing chains. Continued functionalization and polymerization

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reactions in one-pot yield low-polydispersity dendritically branched polymers that do not require any intermediate purification steps. The structure of the products can be varied from star polymers where the arms are linked around a hyperbranched core to hyperbranched polymers with significant molecular weight between branch points. We herein describe this method for the formation of branched polystyrenes and the characterization of the products. Some of our results in characterizing the dendritically branched polystyrenes are interpreted within the framework of a kinetic model that accounts for the distribution of species as a result of steric hindrance on the rate constants.

Experimental Section

Materials. Styrene, *p*-chlorostyrene, and dichlorodimethylsilane were obtained from Aldrich. They were dried over calcium hydride and distilled at atmospheric or under reduced pressure immediately before use. *sec*-Butyllithium in a mixture of cyclohexane and heptane was donated by FMC and used as received. The effective molarity of the solution was determined to be 0.66 M by repeated initiation and polymerization of styrene and the subsequent measurement of the average molecular weights obtained. HPLC grade tetrahydrofuran (THF) was obtained from Fisher, dried over sodium, and distilled from sodium benzophenone ketyl immediately prior to use. Cyclohexane from Fisher was purified[30] and distilled from sodium metal just prior to use. All reactions were conducted under an inert argon atmosphere. Glassware was oven-dried for at least 24 h, flame-dried, and cooled under argon prior to use.

4-(Chlorodimethylsilyl)styrene (CDMSS). CDMSS was prepared by a Grignard reaction involving *p*-chlorostyrene and dichlorodimethylsilane in THF in a manner similar to the procedure reported by Kawakami[31] with some modification. Magnesium turnings (10.00 g, 0.411 mol) were added to a three-neck, round-bottom flask equipped with an addition funnel and condenser. Under an inert argon atmosphere, 20 mL of THF was added along with a few drops of 1,2-dibromoethane. *p*-Chlorostyrene (28.88 g, 0.208 mol) in 70 mL of THF was added dropwise from the addition funnel while maintaining a reflux of THF by external heating. The *p*-chlorostyrene was added over 2.5 h, and the reaction remained at reflux for a further hour. The Grignard reagent was separated from the residual magnesium, transferred by cannula to an addition funnel, and added dropwise over 40 min to an ice bath cooled solution of dichlorodimethylsilane (53.8 g, 0.417 mol) in 30 mL of THF. The reaction stirred for another hour at which time the salts were filtered and the THF was removed by rotary evaporation. The product was distilled under vacuum (0.2 mmHg) at 60−65 °C to yield 27.8 g (68%). The CDMSS was redistilled under vacuum immediately prior to use.

Determination of Anion Stability in THF. Cyclohexane (200 mL) and styrene (2.5 mL, 21.8 mmol) were charged to a dry, rubber septum-sealed, argon-purged, 250 mL round-bottom flask containing a glass-coated stir bar. The solution was titrated with 0.66 M *sec*-butyllithium to a pale yellow color indicative of the styryllithium. The full *sec*-butyllithium initiator charge (4.0 mL, 2.64 mmol) was then injected. After 1 h at room temperature, a 10 mL sample was removed and added directly to argon-purged methanol. The sample was isolated by evaporation of the methanol and cyclohexane and the molecular weight characterized by GPC-MALLS. Forty milliliter portions of the bulk solution were transferred into four separate dry, rubber septum-sealed, 100 mL round-bottom flasks containing glass-coated stir bars. The four separate flasks were labeled A, B, C, and D. To flasks A and C was added 10 mL of THF. Styrene (5.0 mL, 43.6 mmol) was added via syringe pump at the rate of 1 mL/h to flasks A and B. Upon complete addition, the reactions were terminated by the addition of a few drops of argon-purged methanol. After 5 h, styrene (5.0 mL) was added all at once to flasks B and D while cooling with an external water bath. After 30 min, the reactions were terminated with a few drops of argon-purged methanol. The resulting polymers from each reaction were precipitated in methanol and isolated by evaporation of the solvents. The molecular weights were then characterized by GPC-MALLS.

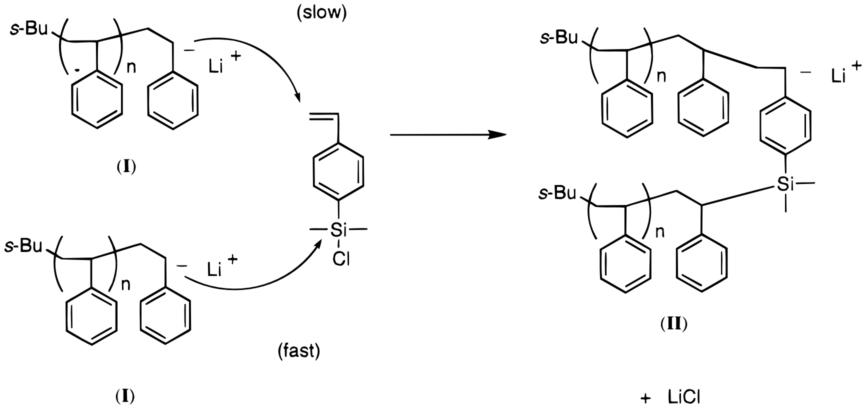
Polymerization. Dendritically branched polystyrenes were synthesized by first forming a living linear polystyrene oligomer of approximately 1150 g/mol and then subsequently coupling chains in a convergent process. All reactions were done at room temperature. A typical procedure employed in synthesizing the dendritic polymers in this study is as follows: styrene (2.0 mL, 17.5 mmol) was charged to a dry, rubber septum-sealed, argon-purged, 100 mL round-bottom flask containing dry cyclohexane (40 mL) and a glass-coated magnetic stir bar. Using a syringe, the solution was then titrated with 0.66 M *sec*-butyllithium to a pale yellow color indicative of the styryllithium. The full *sec*-butyllithium initiator charge (2.4 mL, 1.58 mmol) was then injected. After 30 min, 10 mL of THF was added via syringe, and the reaction mixture took on a deep red color. A sample (1 mL) of the linear oligomer solution was typically removed by syringe at this time and terminated and precipitated by adding directly to argon-purged methanol. This sample was later isolated by evaporation of the methanol and characterized by molecular weight analysis. The reaction of the bulk mixture was continued by adding CDMSS (either alone or mixed with styrene in a calculated ratio to prepare the two different types of structures) at a slow rate by means of a syringe pump until the red color of the polystyryllithium disappeared. At the end of the addition, a few drops of argon-purged methanol were added to ensure termination of any unlikely remaining living chains. Solvent was then removed by rotary evaporation, and the residue was dissolved in CH_2Cl_2 to make a 5% (w/v) solution. The solution was subjected to repeated water extractions to remove LiCl. The product was then concentrated to about 10% (w/v) by rotary evaporation and precipitated by slow addition of the resulting solution to a 10-fold excess of stirred methanol. The white powder was isolated by filtration and subsequently dried under vacuum.

Characterization. Molecular weights were determined by gel permeation chromatography (GPC) coupled with a multi-angle laser light scattering (MALLS) detector. GPC was performed on a Hewlett-Packard model 1084B liquid chromatograph equipped with two Hewlett-Packard PLgel 5 μm Mixed-D columns either in series or in combination with a Waters Styragel HT 4 column for higher molecular weight samples. Elutions were carried out at ambient temperature with THF as solvent at a flow rate of 0.70 mL/min. The MALLS detector was a Wyatt Technology miniDAWN, and the molecular weight characterization software (Astra) was supplied by Wyatt Technology. Peak areas were chosen on the basis of the width of the light scattering peak. The refractive index increment (d*n*/d*c*) for the samples was determined by integration of the refractive index peak of a calibrated RI detector. The value for d*n*/d*c* was found to be 0.193 mL/g for dendritic polystyrene in THF, which corresponds to that of linear polystyrene.[32] This value was used for all calculations. Intrinsic viscosities were measured in THF at 30 °C using a size 50 Cannon-Ubbelohde viscometer. UV−vis spectroscopy was performed using a Perkin-Elmer Lambda 11. Characterization of glass transition temperatures was carried out by differential scanning calorimetry using a Perkin-Elmer DSC-7 running Pyris software. Heating rates were 10 °C/min, and measurements were carried out under an argon purge. T_g was taken as the midpoint of the inflection as determined by the baseline tangents. ^{29}Si NMR spectroscopy was performed with a Chemagnetics CMX Infinity 400. Samples were dissolved in deuterated chloroform with a small amount of added $Cr(acac)_3$ as a paramagnetic relaxation reagent to decrease the long spin−lattice relaxation times.[33] Tetramethylsilane was used as an external reference.

Results and Discussion

Synthetic Method. The reaction sequence that we have devised to form dendritically branched polystyrene

Scheme 1. Reaction of Living Chain Ends with a Deficiency of Coupling Agent



involves the continuous formation and polymerization of vinyl-functionalized polymers or macromonomers. Macromonomers[34,35] can be synthesized by the direct termination of living polymers with a functionalized reactant, and this is the technique utilized here. In a typical macromonomer synthesis, each mole of living chain end is reacted with 1 mol of a functionalized reactant that can couple with the living end to yield a functionally terminated chain end. Vinyl-functionalized macromonomers can be synthesized in this way, provided that the vinyl group of the functionalized reactant does not react with the living chain end or that the reaction with the vinyl group is relatively slow. Vinylbenzyl chloride (VBC) and 4-(chlorodimethylsilyl)styrene (CDMSS) are vinyl-functionalized reactants which have been used to produce macromonomers by their direct reaction with living anionic polymers.[31,36] Previous research has shown that the nucleophilic substitution reaction of polystyryllithium with chlorosilyl[37] and chloromethyl[36] groups is much faster than the addition reaction to the vinyl group, allowing the use of these compounds in the synthesis of macromonomers. Although the reaction stoichiometry requires 1 mol of living chain end for each mole of functionalizing compound, such macromonomer syntheses where the vinyl group is potentially reactive have been accomplished by using an excess of the functionalized reactant in order to avoid any addition to the double bond.[36]

If rather than using an excess of reactant with living polystyrene a deficiency is added, then the macromonomers that form will eventually react through their double bonds with remaining living chain ends to yield dimerized chains and a new living end at the junction point (Scheme 1). The reactant in this case acts as a coupling compound, joining chains together. Such a reaction has been reported by other researchers using CDMSS to make branched block copolymers of polystyrene and polyisoprene.[37] These researchers realized that branching would continue in a dendritic fashion through further reaction with the coupling agent, reporting one such example of low generational growth.

In our approach, we have developed a synthetic strategy of *slow and continuous* addition of a stoichiometric amount of coupling agent to a solution of living polystyrene. The reaction proceeds such that the macromonomers that initially form can react through the vinyl bond with another living end to dimerize with the formation of a new living chain end. This new living chain end can then substitute halide on added reactant to form a new macromonomer. This product can be considered to be the first generation in the convergent process. Because an excess of living chains remain, the sequence of reactions is repeated as more coupling agent is *slowly* introduced to the reaction mixture. This can continue without termination until the molar amount of added coupling agent equals that of original living chain ends, resulting in a convergence in the number of living chain ends and ultimately a dendritically branched core structure with the original linear chains forming the exterior of the macromolecule. As a one-to-one ratio of coupling agent to initial chain ends is reached, termination occurs, and the dendritically branched polymer itself becomes a macromonomer. The rate of addition in the convergent process is an important factor as it needs to be slow enough to allow the reaction of each previous charge of coupling agent at both reactive sites; otherwise, the faster substitution reaction will result in low dendritic growth and prematurely terminated polymers. It was determined that 5 h was slow enough to allow dendritic growth to high generations without being excessively long to allow termination of the chain ends through side reactions. Although this sequence of reactions utilizes an overall one-to-one stoichiometric ratio as in traditional macromonomer formation, the resulting structure is quite different from a typical macromonomer.

While the polymerizability of macromonomers relative to simple monomers has been a much debated topic,[34,38] homopolymerization has been accomplished for vinylbenzyl terminated polystyrene through anionic polymerization to yield a degree of polymerization of 32.[39] Other examples exist for homopolymerization of macromonomers to significant degrees of polymerization,[38] indicating the feasibility of in-situ macromonomer polymerization.

The dendritically branched polymers synthesized in this work are polystyrene-based materials. The coupling agent can be any compound that contains a polymerizable vinyl bond that can maintain living character and a moiety capable of quantitative coupling. We have investigated both CDMSS and VBC as coupling agents and herein report the results for CDMSS.

Two different types of dendritically branched polystyrenes have been synthesized by this general method. The first type is the result of linear polystyrene chains reacted with CDMSS. The resulting polymers can be described as stars where the core is hyperbranched. The second type is the result of reaction of the linear living polystyrene with CDMSS plus styrene monomer. Here, the molecular weight between branch points is dependent on the ratio of CDMSS to styrene, and the materials

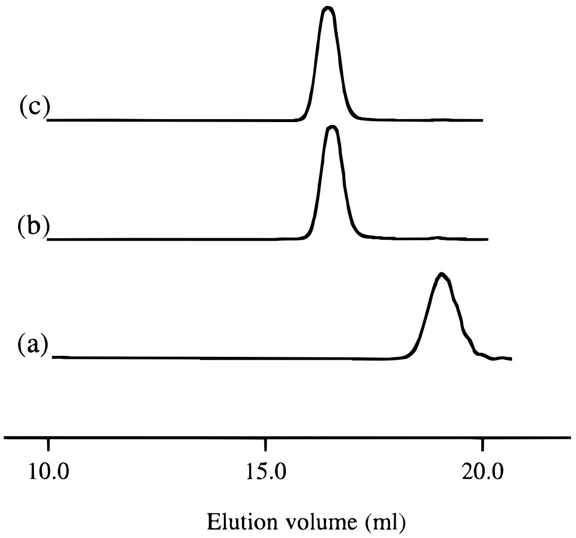


Figure 1. Comparison of GPC chromatograms to demonstrate the stability of the anionic chain end in 20% (v/v) THF: (a) initial chain, (b) result of polymerization in cyclohexane, and (c) result of polymerization in 20% (v/v) THF.

deviate from star-shaped as the ratio and the molecular weight between branch points increase.

For each type of dendritically branched polystyrene synthesis, THF (20% (v/v)) was used to increase the rate of reaction with the coupling agent. Since it is known that THF can participate in a side reaction with butyllithium[40,41] and with polystyryllithium at high concentrations of THF,[42,43] we examined the stability of the living chain end under our reaction conditions by two different experiments. Polystyryllithium (M_n = 830 g/mol) was prepared in cyclohexane at room temperature. In the first experiment, equal amounts of the polystyryllithium solution were placed into two separate flasks. THF (20% (v/v)) was added to one of the flasks, and styrene was added slowly to each of the flasks over a 5 h period. After termination and isolation, the polymers were analyzed by GPC. The chromatograms of the initial chain (a), the polymer from polymerization in cyclohexane (b), and the polymer from polymerization in 20% THF (c) are shown in Figure 1. Figure 1 shows that no significant amount of termination is occurring in the reaction since no low molecular weight tail as the result of such termination can be observed.

A second experiment was performed in which equal amounts of living polystyryllithium (M_n = 830 g/mol) solution prepared in cyclohexane at room temperature were placed into two separate flasks. Twenty percent (v/v) THF was added to one of the flasks, and after 5 h styrene was introduced to each of the flasks. The resulting polymers were terminated, isolated, and analyzed by GPC. The molecular weight analysis of the two samples showed no termination of the initial chains over the course of 5 h, as evidenced by a lack of residual initial chain in the chromatograms. The growth of the polymer upon addition of the styrene led to the same molecular weight with and without THF (M_n = 6800 and 6600 g/mol, respectively, and polydispersity = 1.02 in each case). The resulting GPC chromatograms are identical in appearance to those shown in Figure 1. We conclude from these experiments that although some termination is possible in the presence of THF, very little occurs over the course of 5 h at room temperature for a 20% solution in cyclohexane.

Synthesis and Characterization of Polystyrene with a Hyperbranched Core. Living oligostyrene chains were first synthesized by initiation with *sec*-butyllithium in cyclohexane followed by the addition of THF to increase the rate of propagation. The molecular weight of the initial chains can be controlled and designed to be any length simply by changing the ratio of monomer concentration to initiator concentration. For this work, the molecular weight of the initial chains has been maintained close to 1000 g/mol with the actual values determined by GPC-MALLS characterization of extracted samples. The coupling agent was added slowly over the course of 5 h via syringe pump to the oligostyryl anions thus produced. The polymers were isolated by precipitation and characterized (Table 1).

Schemes 1 and 2 depict the decrease in the total number of living chain ends as the polymerization proceeds. During the course of slow addition of coupling agent, the color of the reaction mixture is observed to fade from initial deep red (due to the high concentration of polystyryl anions) to colorless at the end of reaction. This is representative of the decrease in number of living chain ends as the reaction proceeds. Precipitation of LiCl is also observed with the progression of the reaction, indicative of the nucleophilic substitution reaction. Because of steric reasons, the addition of living dendritic molecules to vinyl-functionalized dendritic molecules is presumed to eventually become slower than the rate of coupling agent addition. The nucleophilic substitution reaction with the CDMSS therefore becomes favored over continued dendritic growth, resulting in the cessation of growth and complete reaction of all living ends in the formation of vinyl-functionalized polymers. The existence of the double bond has been observed for the samples by UV−vis spectroscopy, and the amount of functionalization is found to be nearly quantitative. These vinyl-functionalized polymers can be subsequently used as macromonomers to synthesize unique graft copolymers, and the results of this work will be reported in a subsequent publication. Some similarity in structure can be drawn between these polymers and those obtained by reaction of living polystyrene with divinylbenzene.[44,45] The real difference is in the convergent method, which results in a decrease in the number of anions as the reaction proceeds and does not lead to crosslinking. This allows for the formation of star-shaped macromonomers and the copolymerization with other monomers.

Because of the expected shape difference relative to linear polystyrene, it was expected that GPC of these highly branched polymers relative to linear standards would not yield reasonable molecular weight results. Molecular weight characterization of the polymers was accomplished by GPC coupled with MALLS in order to obtain absolute molecular weight data. GPC chromatograms comparing the initial chain with the final branched polymer (run 6, Table 1) are presented in Figure 2.

The average molecular weights of the products and the average molecular weights of the starting chains allow for the calculation of the average number of generations of the core as demonstrated by the following equations:

$$M_G = 2^G(M_0 + M_B) \tag{1}$$

$$G = \frac{\log(M_G) - \log(M_0 + M_B)}{\log 2} \tag{2}$$

Table 1. Characterization of Star-Shaped Polystyrenes with Hyperbranched Core Synthesized by Slow Addition of Coupling Agent

run no.	M_n of initial chain (g/mol)	$M_w/M_n{}^a$ of initial chain	$M_n{}^a$ (g/mol)	$M_w/M_n{}^a$	av generation no.[c]	$T_g{}^d$ (° C)	[η] 30 °C, THF (dL/g)
1	1690[a]	1.10	15 500	1.17	3.1	68	0.05
2	1060[b]		12 000	1.19	3.3	64	0.06
3	1150[b]		11 400	1.15	3.1	61	0.06
4	1150[b]		12 000	1.17	3.2	63	0.05
5	1020[a]	1.14	11 300	1.15	3.2	60	0.06
6	940[a]	1.10	12 000	1.15	3.4	75	0.06

[a] Molecular weights determined by GPC coupled with multiangle laser light scattering detection. [b] Theoretical values (reaction was not sampled to determine actual molecular weights). [c] Calculated from eq 2. [d] 10 °C/min heating rate.

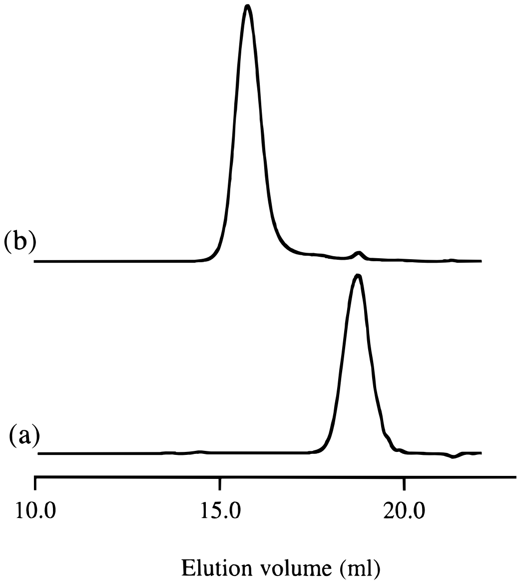


Figure 2. Gel permeation chromatograms of sample run 6 demonstrating the increase in molecular weight and the relatively low polydispersity of the resulting product: (a) initial linear chain; (b) polystyrene with hyperbranched core.

where G equals the average number of generations, M_G equals the number-average molecular weight of the Gth generation, M_B equals the molecular weight of the residue from the coupling agent, and M_0 equals the number-average molecular weight of the starting chains. The average number of chain ends can be calculated as 2^G.

The species depicted in Scheme 2 show that the hyperbranched polymerization can yield a number of products. The nucleophilic substitution reaction of the coupling agent can occur with any reactive anion in the mixture, dependent only on steric inhibitions. Furthermore, the reaction of a living end with a formed macromonomer can also occur between any two appropriately functionalized species within the reaction mixture, again with only steric inhibitions directing the reactions. Therefore, "defects" formed as different generations combine can occur throughout the polymerization resulting in a variety of branched structures. The combination of two units of reactive species **II** with CDMSS would result in second generation anion **IV**, while combination of **I** and **II** with CDMSS would yield **III** as one possible product. Further pairings of the formed species in combination with CDMSS result in the formation of the other structures shown in Scheme 2. Compounds **IV** and **V** have the same molecular weight and number of chain ends and, after termination by reaction with CDMSS, are calculated as the same average generation by eq 2. Continuation of the reactions results in the formation of higher generation structures, and termination of all reactive species occurs as a stoichiometric amount of CDMSS is reached.

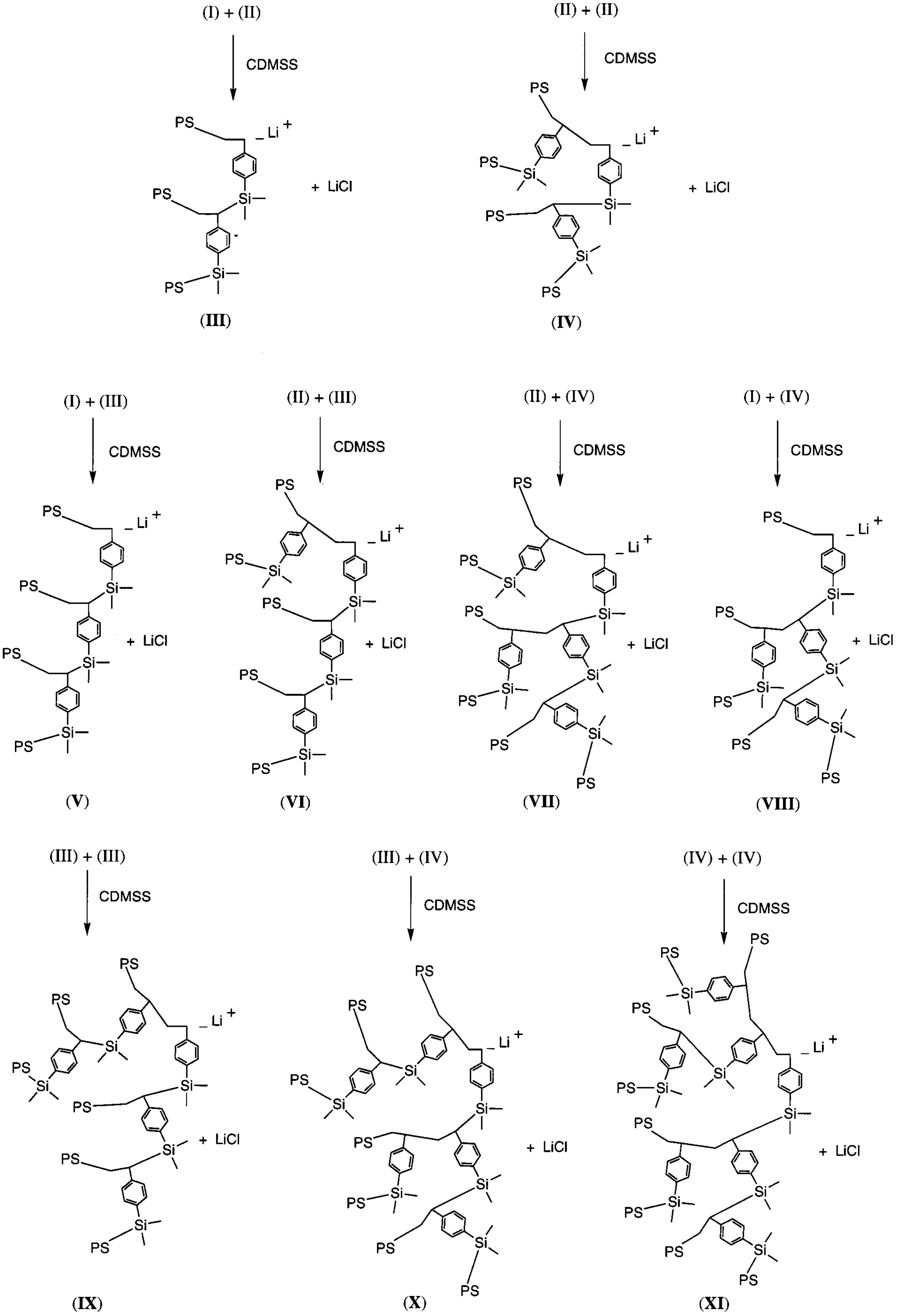
Although different branching architectures are expected, and some of the structures have some linear character to them, each of the expected structures is determined to be fully reacted with respect to substitution of the silyl chloride. ^{29}Si NMR has been used to detect only one type of Si with a chemical shift at −2.8 ppm. Each of the Si atoms of a fully reacted structure is in a similar environment, being attached to an aromatic ring, two methyl groups, and a polystyrene-like chain. If the vinyl group reacts before the silyl chloride, another living chain end can still substitute for halide to result in the hyperbranched structure. Methanol is added to the reaction upon complete addition of coupling reactant and would substitute for halide on any remaining Si−Cl groups. ^{29}Si NMR shows neither Si−Cl groups at 19.8 ppm nor Si−OCH$_3$ groups at the expected resonance of 9.1 ppm (determined by ^{29}Si NMR spectroscopy on CDMSS and the reaction product of CDMSS with methanol, respectively), indicating complete reaction and therefore quantitative branching.

The characterization results listed in Table 1 demonstrate the eventual termination of the chain growth at an average number of generations between 3.1 and 3.4. Termination is presumably due to the steric hindrance around the reactive site allowing only the faster substitution reaction with added coupling agent on the time scale of the continuous addition of reactant.

This description of the dendritic polymerization reaction illustrates the type of growth steps that may occur during synthesis. The kinetics, as well as the distribution of final branched architectures, can therefore be fairly complicated. The direct measurement of the reaction rates in this polymerization is difficult as reactant is slowly added and the structures are continually changing. We discuss the distribution below within the context of a simplified model which accounts for kinetic rates that depend on the architecture of the reacting species.

Kinetic Model. We consider a simple model for the growth kinetics of the dendritic polymers based on the reaction steps as presented in Schemes 1 and 2, including the steps that combine molecules of different molecular weight and/or architecture (branch structure). In principle, the rate constants can depend on both reactant molecular weight and architecture, since we expect the accessibility of the reactive sites to be sterically screened to different degrees depending on the number and location of other monomeric groups on the same molecule. In particular, as the dendritic polymer grows, we expect the rate constant for addition at the active site to decrease.

Scheme 2. Reaction and Example of Possible Structures Obtained from the Slow Addition of CDMSS to a Living Polystyrene Solution



Herein, however, we simplify by considering only explicit dependence on the molecular weight, expecting steric screening to be primarily determined by the sheer number of surrounding monomeric groups from the same molecule. We therefore consider the quantity $c(L,t)$, which represents the total number density of molecules with degree of polymerization L at time t, and the kinetic equations

$$\frac{\mathrm{d}}{\mathrm{d}t}c(L,t) = \frac{1}{2}\sum_{n=1}^{L-1}[k_{n,L-n}c(n,t)\,c(L-n,t)] - c(L,t)\sum_{n=1}^{\infty}k_{n,L}c(n,t) \quad (3)$$

where for $L = 1$ the first sum is zero. The first sum represents the various combinations of an n-mer with an $(L\text{-}n)$-mer that react to form an L-mer, while the second sum accounts for the depletion in the population of L-mers from reaction with any other n-mer. We only consider reactions between a living chain end and a macromonomer and neglect the relatively fast nucleophilic substitution reaction of a living chain end with the coupling agent. For the present case of very slow addition of coupling agent, the time "t" is actually a dummy variable that depends only on the extent of reaction, since the reaction proceeds incrementally only as coupling agent is added.

We consider two cases. First, we review the case where the rate constants $k_{n,m}$ are independent of n and m. Here, the kinetics are essentially linear AB polycondensation-like,[18] and we have a uniform statistical distribution of branch architectures. Second, we will consider numerically models for the rate constants $k_{n,m}$ which decrease with increasing n and m, reflecting the increased steric screening.

Case I: Size-Independent Rate Constant $k_{n,m} = k$. In this case, we assume that the reaction rate is independent of the size and architecture of the combining species. Equation 3 then reduces (neglecting even−odd effects) to

$$\frac{\mathrm{d}}{\mathrm{d}t}c(L,t) = \frac{1}{2}k\sum_{n=1}^{L\text{-}1}[c(n,t)\,c(L-n,t)] - kc(L,t)\sum_{n=1}^{\infty}c(n,t) \quad (4)$$

This infinite set of nonlinear differential equations can be solved exactly by Laplace transformation. For initial conditions of the reaction pot containing only monomers at polymer (number) density $c(L{=}1,t{=}0) = c_{\mathrm{M}}$, we find the various time-dependent L-mer populations to be

$$c(L,t) = \frac{4c_{\mathrm{M}}}{(c_{\mathrm{M}}kt)^2}\left(\frac{c_{\mathrm{M}}kt}{c_{\mathrm{M}}kt + 2}\right)^{L+1} \quad (5)$$

an exponential distribution in size, but with a power-law decay in time. The normalized distribution of weight, $(c/c_{\mathrm{M}})L$, as well as the polydispersity is shown at various times in Figure 3. It can be easily verified that the moments of the distribution $c(L,t)$ are given by

$$S_0 = \sum_{L=1}^{\infty}c(L,t) = \frac{2c_{\mathrm{M}}}{c_{\mathrm{M}}kt + 2} \quad (6)$$

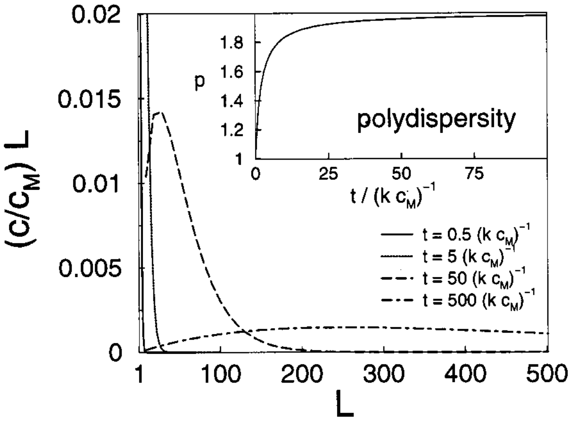


Figure 3. Population weight distribution of L-mers at times $t = 0.5$, 5, 50, and 500 (in units of $(kc_{\mathrm{M}})^{-1}$), for the case of molecular weight-independent rate constant k (no steric inhibition). Inset shows polydispersity (p) versus time (t).

$$S_1 = \sum_{L=1}^{\infty}Lc(L,t) = c_{\mathrm{M}} \quad (7)$$

$$S_2 = \sum_{L=1}^{\infty}L^2c(L,t) = c_{\mathrm{M}}(c_{\mathrm{M}}kt + 1) \quad (8)$$

The first sum counts the number of reactive species remaining at time t and indicates second-order kinetics, while the second sum expresses the conservation of mass (total monomer number). Note that the extent of reaction, A, is simply

$$A = \frac{S_0(0) - S_0(t)}{c_{\mathrm{M}}} = \frac{c_{\mathrm{M}}kt}{c_{\mathrm{M}}kt + 2} \quad (9)$$

and corresponds to the amount of coupling agent that has been slowly added. (A is the fraction of coupling agent added relative to the amount needed for the reaction to go to completion.) The third sum exhibits a linear growth and therefore implies a linear growth in the number- and weight-average molecular weights, which are proportional to the ratios $S_1/S_0 = c_{\mathrm{M}}kt/2 + 1$ and $S_2/S_1 = c_{\mathrm{M}}kt + 1$, respectively. The polydispersity p can thus be seen to increase steadily from $p = 1$ at the initial time (unreacted monomer) to its asymptotic value of $p = 2$ for large t (when the distribution is essentially exponential). Expressed in terms of the extent of reaction, the polydispersity is simply

$$p = (S_2/S_1)/(S_1/S_0) = A + 1 \quad (10)$$

To determine the distribution of branched architectures in this case, it is useful to note that the number of L-mers that are formed from the reaction of an n-mer and a $(L - n)$-mer is completely independent of n, as can be verified explicitly by direct substitution. Because the formation of an L-mer is equally likely from any pair $(n,L - n)$ at all times, the distribution at any time is also equally likely from any such pair. If we consider a branch point in an L-mer as a partition between two branches with a total of L monomers, then every partition is equally likely. In this sense, the branch structure is completely statistical.

The main conclusion, then, for the formation of dendritically branched polymers by this method is that,

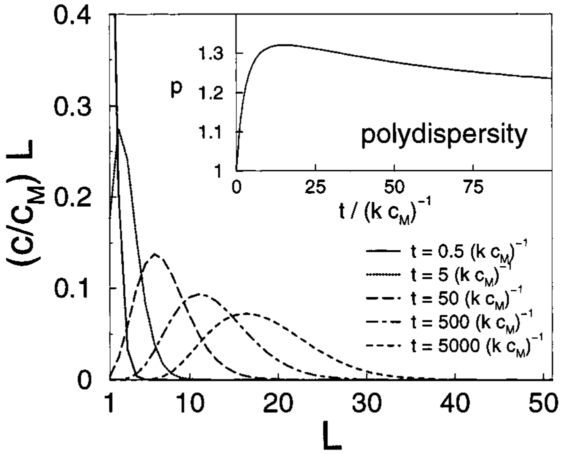


Figure 4. Population weight distribution of L-mers at times $t = 0.5$, 5, 50, and 500 (in units of $(kc_M)^{-1}$, with k taken to be the rate constant for monomers, k_0), for the case of exponentially decaying rate constant k (steric inhibition). Inset shows nonmonotonic polydispersity (p) versus time (t).

in the absence of size dependence in the rate coefficients (e.g., due to steric exclusion effects), the reaction kinetics are essentially AB condensation kinetics, with a completely statistical distribution of branch partitions. Notably, even in this case, the expected polydispersity is 2 rather than the extremely broad values calculated for other hyperbranched polymerizations.[17,18,23]

Case II: Size-Dependent Rate Constants $k_{n,m}$. The particular form for the rate constant $k_{n,m}$ depends on the relative accessibility and reactivity of the reactive sites on the n-mer and the m-mer. Since the branch points in a given macromonomer are fairly close together (in the case of dendritic polymerization without added comonomer), we anticipate that the steric exclusion increases rapidly as the branch content increases. We have examined a few particular models but here illustrate the "focusing" effect of size dependence in the rate constant by considering the exponential case of

$$k_{n,m} = k_0 e^{-(n+m)/\lambda} \tag{11}$$

where k_0 is a constant prefactor and λ is an exponential constant characterizing the typical size above which reactions are exponentially difficult. This model might be justified in terms of an activation free energy penalty for overlapping an increasing number of monomers in the same spatial region.

We have solved eq 3 numerically, with the exponential model for the rate constant given in eq 11, using as parameters $k_0 = 1$ and $\lambda = 4$. Starting with an initial monomer number density of c_M, we find that the distribution of L-mers is initially somewhat exponential (before the monomers feel the effect of the exponential damping) but then quickly becomes focused into a narrow distribution with falling polydispersity, as shown in Figure 4. For time $t = 500(kc_M)^{-1}$, we see that there is now a peak in $c(L,t)$ corresponding to an 11-mer and that the polydispersity, after initially increasing, returns to a value of about 1.14 (outside of the range of the inset—but see Figure 5a). These values are very close to the experimental values in Table 1. The effect of focusing due to steric inhibition, as compared to case I without steric inhibition, is further highlighted by Figure 5b, which shows the polydispersity first increasing and then decreasing with extent of reaction A or with average degree of polymerization $\langle L \rangle$.

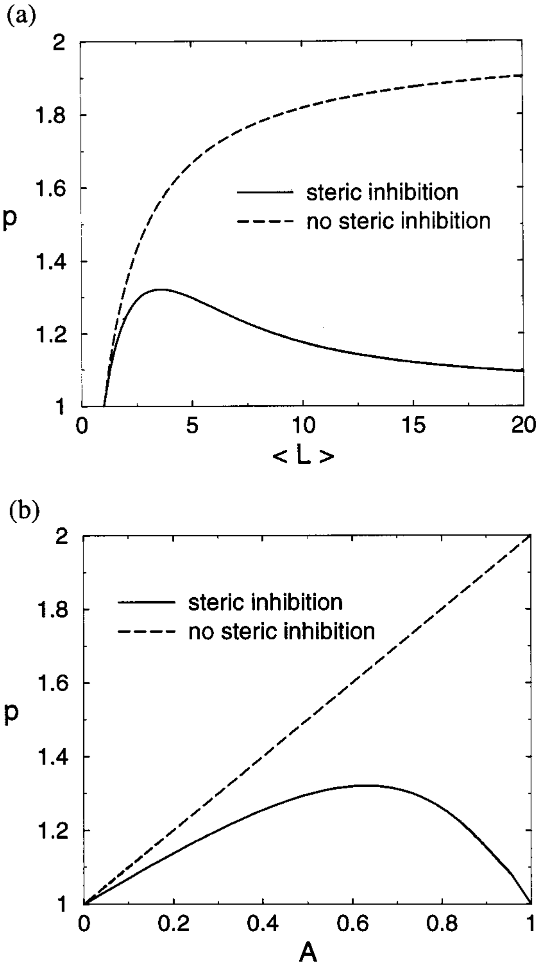


Figure 5. Comparison between the cases of steric inhibition and no steric inhibition: (a) polydispersity (p) versus number-average degree of polymerization (L); (b) polydispersity (p) versus extent of reaction (A). Values of k_0 and λ are as given in the text.

The main conclusion, then, for the case of decreasing reaction rate with size is that *since the larger generation materials experience a decrease in reaction rate, the smaller generation materials can preferentially react and "catch up" to the larger ones.*

This model calculation serves primarily to show that the slowing down of reactions due to size can approximate the size and polydispersity observed experimentally. Furthermore, the crudely estimated value of λ seems to be in a reasonable range for the model of a steric activation free energy-controlled rate constant. The details of the population distribution profile (such as the asymmetry of the shape) will depend on refinement of the rate constants, as well as matching experimental conditions. For instance, experimentally, the profile is seen to have a sharper edge at higher size and a more diffuse edge at lower size. This can be related to factors such as competing early termination of the reaction, which have not been accounted for within the current model.

Increased Molecular Weight between Branch Points. It is known from the previous reactions that the dendritic anion can react with the dendritic macromonomer but that reaction is expected to decrease in rate as the size of the dendritic molecules increases. To decrease the steric problems which limit the growth of the dendritic core, styrene was introduced along with the coupling agent in molar ratios of approximately 5:1,

Table 2. Characterization of Dendritic Polystyrenes with Increased Molecular Weight between Branch Units by Variation of Coupling Agent to Styrene Ratio

run no.	coupling agent: styrene ratio	$M_n{}^a$ of initial chain	$M_w/M_n{}^a$ of initial chain	$M_n{}^a$ of dendritic polymer (g/mol)	$M_w/M_n{}^a$	av generation no.^{c}	$T_g{}^d$ (°C)	[η] 30 °C, THF (dL/g)
7	1:5	2130	1.05	62 000	1.13	4.5	89	0.10
8	1:10	1100^b		67 900	1.32	5.0	84	0.10
9	1:10	1150^b		67 700	1.34	5.0	84	0.10
10	1:10	620	1.15	94 400	1.24	5.8	81	0.11
11	1:10	1510	1.10	70 900	1.28	4.8	90	0.11
12	1:10	950	1.10	87 300	1.22	5.5	89	0.11
13	1:15	1480	1.18	101 000	1.14	5.1	87	0.13
14	1:20	1150	1.10	137 000	1.19	5.4	89	0.15
15	1:20	1480	1.07	176 000	1.21	5.6	91	0.16
16	1:50	1230	1.02	252 000	1.27	5.3	96	0.24
17	1:92	1260	1.04	537 000	1.38	5.6	99	0.41
18	1:137	980	1.07	595 000	1.45	5.3	104	0.52
19	1:146	950	1.08	605 000	1.25	5.2	104	0.53

[a] Molecular weights determined by GPC coupled with multiangle laser light scattering detection. [b] Theoretical values (reaction was not sampled to determine actual molecular weights). [c] Calculated from eq 2. [d] 10 °C/min heating rate.

10:1, 15:1, 20:1, 50:1, 92:1, 137:1, and 146:1 of styrene to coupling agent, respectively. This was expected to produce a statistical increase in the molecular weight between branches. By adding the mixture of CDMSS and styrene slowly and allowing complete reaction of all reactive species before the next addition of reactants, polystyrene chains with molecular weights dependent on the molar ratio relative to coupling agent are expected to be formed around the branch points. The actual average molecular weight between branch points is complex, and the styrene and coupling agent are distributed throughout the structure depending on the molar ratio and reaction rates. Since the styrene and coupling agent are added directly to the initial chains, some continued growth of the linear chains can be expected before coupling begins. This becomes significant as the ratio of styrene to coupling agent increases.

The average number of generations can be readily calculated for these modified dendritically branched polystyrenes using eq 2 where M_B is now defined differently. M_B is calculated as the relative molar amount of styrene multiplied by the molecular weight of a styrene repeat unit (104 g/mol), neglecting the small molecular weight contribution of the residue from the coupling agent. Therefore, a molar ratio of 10:1 styrene to coupling agent yields a M_B equal to 1040 g/mol. This amount of styrene is distributed on average around each coupling agent residue, and M_B can be considered to be the average molecular weight of a branch unit.

This technique resulted in high molecular weight materials with the average number of generations increasing as the quantity of added comonomer, and hence molecular weight of the branches, is increased (Table 2). This increase in the average number of generations is attributed to the relief of steric constraints at the interior of the molecule. Similar methods have been used in the synthesis of true dendrimers where it has been observed that increasing the length between branches permits the synthesis to be carried out to higher generations.[46] As the polymerization of added monomer proceeds, the reactive site is no longer as obstructed, and the coupling reaction can continue. The polydispersities for these samples remain low, indicating a difference from purely statistical combinations of reactive species and efficient crossover between reactive species.

The structure of the branched polystyrenes produced is very different from that produced without added comonomer. While the polymers produced without added comonomer can be compared to star-shaped polymers from reaction with divinylbenzene, the polymers produced with added comonomer are not star-shaped. One can view this as expansion of the core as the amount of added comonomer is increased. The extent of branching was measured by ^{29}Si NMR and was determined to be complete on the basis of no detection of unreacted pendent Si atoms.

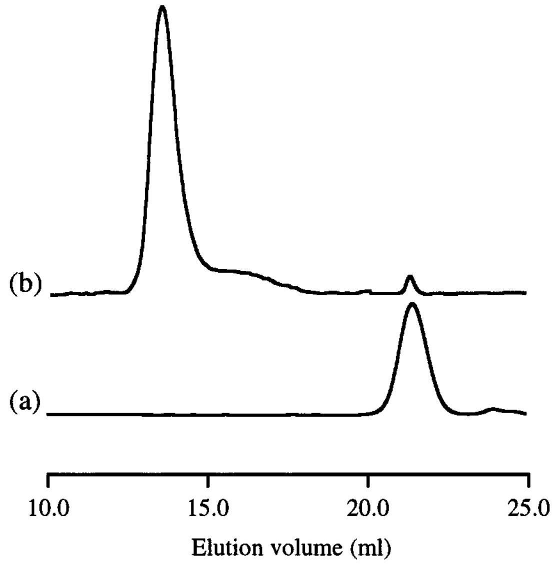


Figure 6. Gel permeation chromatograms of sample run 11 demonstrating the increase in molecular weight and the relatively low polydispersity of the dendritically branched polystyrene: (a) initial linear chain; (b) dendritic polystyrene.

The progress of the polymerization can be observed by GPC-MALLS analysis of the initial chain compared with the final product. Figure 6 depicts the results obtained for one particular sample (run 11, Table 2). The initial linear chain was sampled and found to have a number-average molecular weight of 1510 g/mol and a polydispersity of 1.10. The subsequent slow addition of styrene and CDMSS in a 10-to-1 molar ratio resulted in the dendritic growth. GPC-MALLS analysis of the final product after isolation by precipitation shows the number-average molecular weight to have increased to 70 900 g/mol, while the polydispersity remains relatively low at 1.28. Some low molecular weight tail of the sample is obvious in the GPC chromatogram, most likely a result of a small amount of premature termination

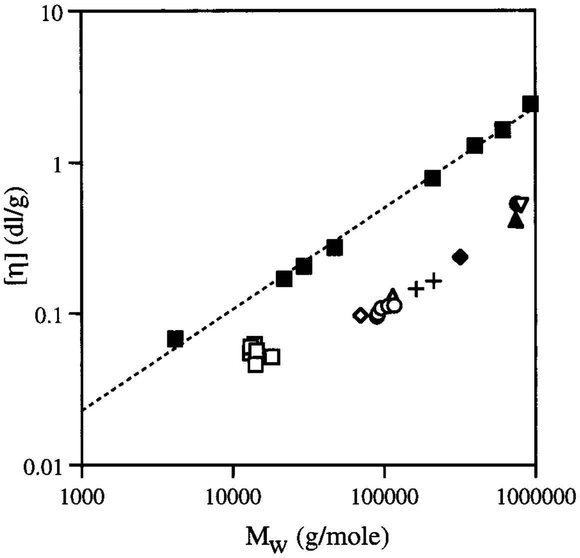


Figure 7. Intrinsic viscosity behavior of dendritically branched polystyrenes compared to linear polystyrene. Linear polystyrene standards (M_w measured by GPC-MALLS) in THF at 30 °C (■, dashed line). Dendritically branched polystyrene in THF at 30 °C with coupling agent-to-styrene ratio: 1 to 0 (□), 1 to 5 (◇), 1 to 10 (○), 1 to 15 (△), 1 to 20 (+), 1 to 50 (◆), 1 to 92 (▲), 1 to 137 (▽), 1 to 146 (●).

by impurities during the continuous slow addition of reactants or other termination side reactions.

Characterization of Solution Viscosity. In contrast to classical linear and branched anionic polymerizations, no appreciable changes in the solution viscosity of the reaction mixtures were detected as polymerization progressed, reflecting the highly branched nature of the polymers and their decrease in the extent of entanglement. A noticeable viscosity increase is observed for comparable linear polymerizations to the same molecular weight. To gain insight into the shape of these highly branched polymers, intrinsic viscosity measurements were performed. The values obtained in THF at 30 °C (Tables 1 and 2) are extremely low compared to linear polystyrenes of the same molecular weight (Figure 7).

Dendrimers have been found to display a maximum in their intrinsic viscosities as a function of molecular weight after which further increases in molecular weight result in a lowering of the intrinsic viscosity.[47−49] This unique behavior has been correlated with the gradual changes in shape from an extended to a more compact globular structure. The nature of less perfect hyperbranched polymers has not been fully elucidated. Early work on hyperbranched polyesters indicated that although hyperbranched materials show a decreased Mark−Houwink exponent compared to linear materials, they do not display a maximum in their intrinsic viscosities.[13,50] More recent experimental work has shown that a maximum intrinsic viscosity behavior similar to dendrimers is observed for some hyperbranched polymers,[51,52] while recent theoretical models of hyperbranched polymers also predict dendrimer-like intrinsic viscosity behavior.[53,54] Arborescent graft polystyrenes[25] and polybutadienes,[28] which can be more readily compared to the structure of the dendritically branched polystyrenes synthesized here, show a leveling off of the intrinsic viscosity with generational growth.

Because the increase in molecular weight of the dendritically branched polystyrenes is attained by increasing the molecular weight between branches, a comparison with the intrinsic viscosity behavior of other materials, where the molecular weight increases solely by an increase in the number of generations, cannot be made. Although the samples with increased molecular weight between branch points are still expected to be more compact than a linear polystyrene of comparable molecular weight, the resulting more flexible structure obtained by increasing the branch length is not expected to be more globular than a lower molecular weight sample. A better comparison to dendrimers would be obtained by synthesizing a homologous structure series where only the number of generations changes, as is done for true dendrimers.

Characterization of T_g. Studies of the thermal behavior of dendritic polymers have shown that the glass transition temperature is dependent on the structure of the polymer backbone and on the nature and number of end functional groups.[55,56] Entanglements are considered to be absent from most dendritic polymers because of their highly branched nature and therefore do not influence the glass transition temperature. The end functional groups play a significant role in determining the glass transition temperature since their concentration does not typically drop off with molecular weight as is the case for linear polymers. The dendritically branched polystyrenes synthesized in this study all contain the same *sec*-butyl end groups and are similar in their backbone structures except for number of branching units. The main variable is the molecular weight relative to the number of end groups, which is altered by changing the molecular weight between branch points. Entanglements are not expected to affect their physical properties since the molecular weight between branches is expected to be less than the entanglement molecular weight for polystyrene (M_e = 18 700 g/mol[57]) in all cases. Thermal investigation of the dendritically branched polystyrenes indicates that the T_g increases with the overall molecular weight and that the relationship can be described by considering the molecular weight relative to the number of end groups in a fashion similar to that done for dendrimers.[55] Although there is significant scatter in the data, the T_g's for the dendritic polymers are observed to follow a linear Fox−Flory[58,59] relationship (i.e., $T_g = T_{g\infty} - K/M$) where M is equal to the number-average molecular weight divided by one-half the number of end groups. (This definition of M is the same as that used for linear polymers where two end groups are found.) The constant K is found to be equal to 9.7×10^4 (correlation coefficient $r^2 = 0.85$) (Figure 8a), which is similar to the value for linear polystyrene (literature value[60] 1.0×10^5). This is a reasonable result considering that the constant K in the Fox−Flory chain-end free volume theory accounts for the free volume due to the end groups, and in this case we have normalized the molecular weight of the dendritic polystyrenes to the same number of end groups as in linear polystyrene. The glass transition temperatures are found to be slightly higher for the dendritic polystyrenes relative to linear polymer, yielding a value of $T_{g\infty}$ equal to 105 °C versus 100 °C for linear polystyrene. The higher T_g's presumably demonstrate the effect of the branch unit on restricting the chain motion. The change in T_g versus M is depicted in Figure 8b, and the slight difference from the behavior of linear polystyrene is apparent.

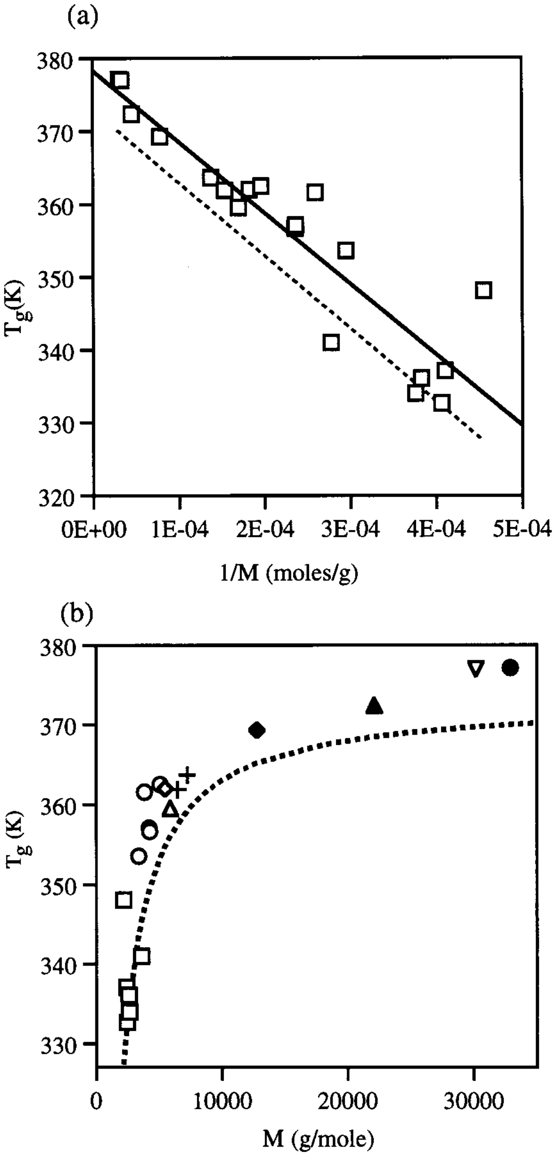


Figure 8. (a) Plot of T_g versus $1/M$ (where $M = 2M_n$/number of end groups) for dendritically branched polystyrene (□) and linear polystyrene[60] (dashed line). (b) Plot of T_g versus M for linear polystyrene[60] (dashed line), and dendritically branched polystyrene with coupling agent-to-styrene ratio: 1 to 0 (□), 1 to 5 (◇), 1 to 10 (○), 1 to 15 (△), 1 to 20 (+), 1 to 50 (◆), 1 to 92 (▲), 1 to 137 (▽), 1 to 146 (●).

Conclusions

This work demonstrates that relatively low-polydispersity dendritically branched polymers can be produced by coupling living polymer chains in a convergent manner using coupling agents that contain both a polymerizable group and a moiety capable of quantitatively coupling with a living chain. The low polydispersities can be understood by modeling the reaction kinetics with the assumption that the reaction rates are dependent on the accessibility of the reactive sites. In particular, a model assuming exponential steric inhibition of the polymerization rate constant is in agreement for the polydispersity and dendritic size relative to experimental measurements.

Using this method, dendritic polystyrenes with different branch lengths have been synthesized and characterized. The average number of generations attained is observed to increase with an increase in the molecular weight between branches. The branched polystyrenes have low intrinsic viscosities and demonstrate glass transition temperatures similar to linear polystyrene relative to the number of end groups. This method is an improvement in synthesis over that of other hyperbranched polymers in that highly branched, low-polydispersity materials can be made in a one-pot reaction without the need for fractionation or other purification at intermediate steps. Furthermore, the living nature of the polymerization allows for numerous modifications. The ability to add functional groups to the chain end and otherwise modify the structure allows for the specific design of many different dendritic polymers. Research on this novel technique to produce other modifications is continuing and will be reported in subsequent publications.

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