

STAR AND HYPERBRANCHED POLYMERS

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Synthesis of Branched Polymers: An Introduction

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I. INTRODUCTION

Major developments in the science and technology of polymeric materials have resulted from the preparation and characterization of polymers with well-defined structures [1,2]. Well-defined polymers with low degrees of compositional heterogeneity can provide the information and insight necessary to understand and predict polymer structure–property relationships. Branching in polymers is a useful structural variable that can be used advantageously to modify the processing characteristics and properties of polymers. A branched polymer is comprised of molecules with more than one backbone chain; that is, it is a nonlinear polymer [3]. A branched polymer is characterized by the presence of branch points (junction points): (atoms or a small group from which more than two long chains emanate) and by the presence of more than two chain end groups.

Branching affects the crystallinity, crystalline melting point, physical properties, viscoelastic properties, solution viscosities, and melt viscosities of polymers [3–6]. However, it is difficult to predict the relationships between branching and properties based on the behavior of most branched polymers because the branching reaction generally occurs in a random fashion. As a con-

sequence, the number and types of branches per macromolecule are difficult to define except on an average basis.

Fundamental understanding of the effects of chain branching on polymer properties requires the availability of a variety of branched polymers with well-defined structures and low degrees of compositional heterogeneity [1,6]. Living chain reaction polymerizations are particularly suited for the preparation of these “model” polymers since it is possible to vary and control important structural parameters such as molecular weight, molecular weight distribution, copolymer composition and microstructure, tacticity, chain end functionality and the number of branches per molecule. Although a variety of mechanistic types of living chain reaction polymerization have been developed [6], living anionic polymerization, especially using alkylolithium initiators, is the paradigm [7] from which examples will be drawn for illustration of the general methods. This review will first consider the general polymerization methods that have been developed to synthesize regular star-branched polymers, heteroarm star-branched polymers, and other types of branched polymers, including graft copolymers [8]. Regular star-branched polymers have a single branch point and all arms exhibit low degrees of compositional heterogeneity with respect to composition, molecular weight, and molecular weight distribution. Heteroarm star-branched polymers [6,9], also described as mikto-arm star polymers [6], also have a single branch point, but the arms differ in either molecular weight or composition. When the arms differ in composition, heteroarm star-branched polymers can be considered as a special type of graft copolymer [8]. Finally, a brief review of dendrimers and hyperbranched polymers will be presented. Dendrimers are highly branched, three-dimensional macromolecules with a branch point at each monomer unit [10–14].

II. SYNTHESIS OF BRANCHED POLYMERS

The methodology of living polymerization is ideally suited for the preparation of well-defined, star-branched polymers and copolymers with low degrees of compositional heterogeneity. Because termination and chain transfer reactions are absent and the chain ends may be stable for sufficient time periods (the laboratory time scale), these polymerizations have the following useful synthetic attributes for star polymer synthesis:

1. One polymer is formed for each initiator molecule, so that the number average molecular weight of polymers or block segments can be predicted from the reaction stoichiometry. Multifunctional initiators with functionality n can form stars with n arms.

2. If the rate of initiation is rapid or competitive with the rate of propagation, polymers (precursor arms) with narrow molecular weight distributions ($M_w/M_n \leq 1.1$) [15] are formed.
3. When all of the monomer has been consumed, the product is a polymer with reactive chain ends that can participate in a variety of post-polymerization reactions:
 - a. block copolymerization by addition of a second monomer, and/or
 - b. end-linking with multifunctional linking agents to form the corresponding star-branched polymers with uniform arm lengths.

In the following sections, the general methods for synthesis of regular star-branched polymers and heteroarm star-branched polymers will be described. Specific examples will be shown based on alkyllithium-initiated anionic polymerization.

A. Postpolymerization, End Linking with Multifunctional Linking Agents

1. General Aspects

The products of living polymerizations are polymers that retain their active, propagating chain ends when all of the monomer has been consumed. Under appropriate conditions, these polymers exhibit well-defined, predictable number average molecular weights and narrow molecular weight distributions, i.e., low degrees of compositional heterogeneity. These living polymers can be reacted with multifunctional linking agents to form star-branched polymers in which the number of arms corresponds to the functionality of the linking agent, as shown in Eq. (1) where P^* is a living polymer chain, $L(X)_n$ is a multifunctional linking agent of functionality n , and $L(P)_n$ is a star-branched polymer containing n arms.



The main advantage of this methodology is that the arms of the resulting branched polymer are well defined because the precursor arms can be characterized independently from the star. Because of the well-defined arms, the number of arms can be readily determined by measuring the molecular weight of the star. In principle, a variety of well-defined, star-branched polymers with different numbers of arms can be prepared using this method by varying the functionality of the linking agents [$L(X)_n$].

2. Anionic Polymerization

A wide variety of multifunctional linking agents have been investigated for preparation of star-branched polymers via anionic polymerization [7,16,17]. Arm functionalities range from 3 to very high values. However, many of the reported linking reactions, such as those involving polyfunctional alkyl halides, are complicated by side reactions such as elimination and metal–halogen exchange that lead to compositional heterogeneity. In contrast, linking reactions with polyfunctional silyl halides are very efficient and free of these complicating side reactions.

a. Polyhalosilanes and Stannic Chloride. One of the most general and useful methods for preparation of star-branched polymers is the reaction of polymeric organolithium compounds with multifunctional electrophilic species such as silicon tetrachloride, as shown in Eq. (2). A slight excess of living arm, PLi, is generally employed to drive the reaction to completion and to minimize the formation of stars with less than the stoichiometric number of arms. This in turn requires that the product be fractionated to obtain pure, star-branched polymer.



These linking reactions are not complicated by side reactions; however, they are sensitive to the steric requirements of the linking agents and the organolithium chain ends. For example, early work by Morton and co-workers [18] showed that the reaction of poly(styryl)lithium with a less than stoichiometric amount of silicon tetrachloride produced a polymer product composed of 26% of the four-armed star and 74% of the three-armed star polymers. More efficient linking can be effected using poly(butadienyl)lithium chain ends. This was illustrated by Zelinski and Wofford [19], who reacted poly(butadienyl)lithium with methyltrichlorosilane and silicon tetrachloride to efficiently form the corresponding three-armed and four-armed, star-branched polymers, respectively. Linking efficiency can also be improved by separating the Si–Cl groups with spacers such as methylene groups to reduce the steric repulsions in the linked product [20].

Linking with multifunctional silyl chlorides has been extended to stars with arm functionalities over one hundred by utilizing the linking reactions of poly(butadienyl)lithium with carbosilane dendrimers containing up to 128 Si–Cl bonds [21]. Star-branched polybutadienes with more than 250 arms were reported for the linking reactions of poly(butadienyl)lithium with the product from hydrosilylation of 1,2-polybutadiene [22].

Fetters and co-workers [23,24] developed a general method for synthesis

of heteroarm star-branched polymers by utilizing the decreased reactivity of poly(styryl)lithium compared to poly(butadieny)lithium in linking reactions with polyhalosilanes. Hetero, three-armed star polystyrenes and polybutadienes were prepared using the reaction sequence shown in Scheme 1. After the first step, the excess methyltrichlorosilane was removed by evacuation. The excess of P'Li in the second step must be removed by fractionation. This method has been extended to a variety of other heteroarm star polymers as detailed in a recent review [6].

The efficiency of postpolymerization linking reactions of polymeric organolithium compounds with polyhalosilanes is utilized in a number of commercial processes [7]. The melt viscosity (high shear) and cold-flow (low-shear) properties of linear elastomers with narrow molecular weight distributions are poor. These limitations are eliminated by postpolymerization branching reactions such as linking with polyhalosilanes [7,25,26].

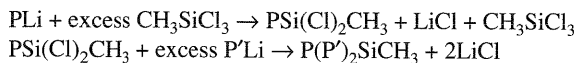
Stannic chloride undergoes linking reactions with polymeric organolithiums analogous to the reactions of silicon tetrachloride, as illustrated in Eq. (3). In addition to the improvement in cold flow and



processing properties expected for a branched polymer, it has been reported that the incorporation of tin-functionalized, star-branched styrene-butadiene rubbers and polybutadienes into formulations with carbon black improved tire performance [27,28].

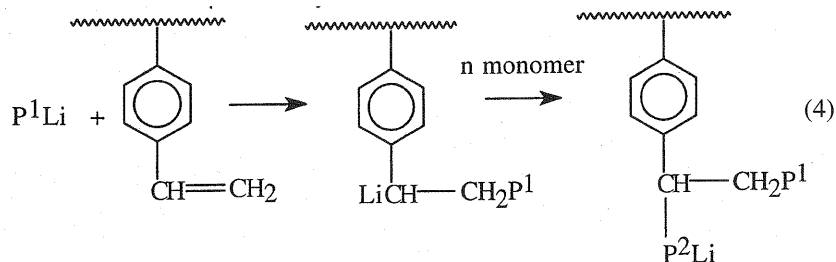
The development of processible, clear, impact-resistant grades of polystyrene for rapid molding operations is also based on end-linking reactions [7]. These polymers (e.g., Phillips K-resins) are mixtures of block copolymers of styrene and butadiene formed by incremental additions of alkylolithium initiator and monomers followed by some form of linking reaction. Linking agents such as aliphatic dicarboxylic acids and polyhalosilanes have been described [7]. An analogous product (BASF Styrolux), which includes butadiene/styrene blocks with a tapered block structure, utilizes an oligofunctional coupling agent to form an unsymmetrical star polymer with about four arms [29].

b. Divinylbenzenes. The copolymerization of styrenes and dienes with difunctional monomers such as divinylbenzene would be expected to form



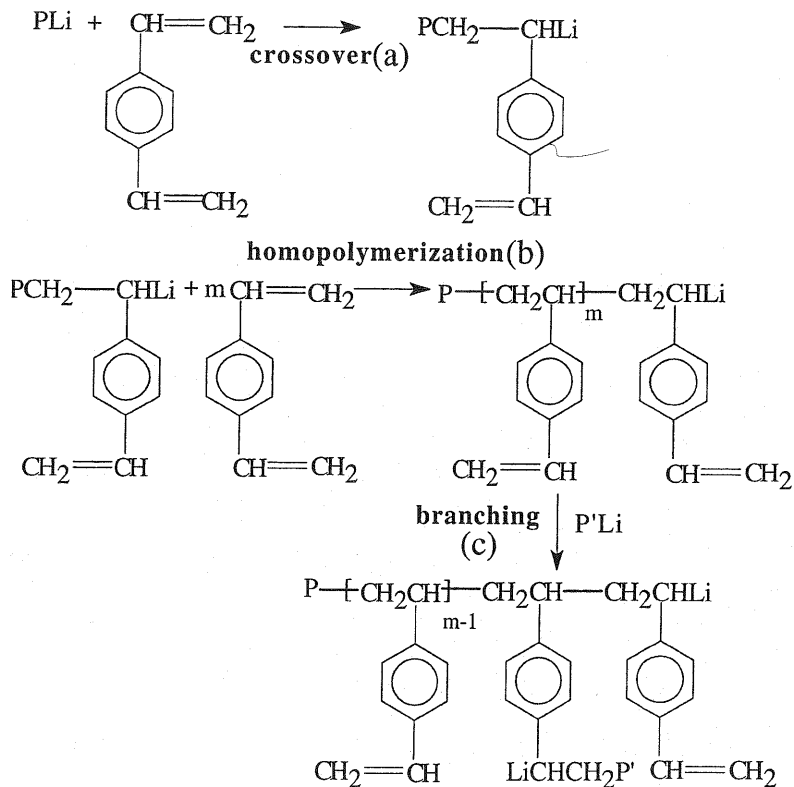
Scheme 1

a gel and the gel point would depend on the monomer reactivity ratios and the relative concentrations of the two monomers [30,31]. The gel point is preceded by the formation of branched molecules that then react with other branched molecules to ultimately form a gel. Thus, if the amount of difunctional monomer were chosen carefully, it would be expected that copolymerization with a difunctional monomer could lead to a branched polymer rather than a gel. Copolymerization of divinylbenzene with dienes or styrene/diene mixtures is used commercially to introduce random long-chain branching during the polymerization process [7,32]. Subsequent to DVB incorporation into a growing chain, other active chains can add to the resulting pendant vinylstyrene units, followed by further monomer addition to generate long-chain branching, as shown in Eq. (4).



As described previously, introduction of branching improves both the cold flow (low shear) and melt viscosity (high shear, processing) properties analogous to the effect of postpolymerization end-linking with polyhalosilanes.

Divinylbenzenes can also be used for postpolymerization end-linking reactions. The linking reactions of polymeric organolithium compounds with divinylbenzenes (DVB) provide a very versatile, technologically important, but less precise method of preparing star-branched polymers. As shown in Scheme 2, the linking reactions with DVB can be considered in terms of three consecutive and/or concurrent reactions: (a) crossover to DVB, (b) block polymerization of DVB, and (c) linking reactions of carbanionic chain ends with pendant vinyl groups in the DVB block [poly(4-vinylstyrene)] [3,7,33,34]. The uniformity of the lengths of the DVB blocks depends on the relative rate of the crossover reaction (a) compared to the block polymerization of DVB, (b) and the linking reactions (c). This block copolymerization-linking process has been described as formation of a DVB microgel nodule that serves as the branch point for the star-shaped polymer [33]. In principle, j molecules of divinylbenzene could link together $(j + 1)$ chains [33]. Although the number of arms in the star depends on the molar ratio of DVB to polymeric organolithium compound, the degree of linking obtained for this reaction is a complex func-



Scheme 2

tion of reaction variables [33–36]. It should be noted that these linking reactions are effected with technical grades of DVB that contain varying amounts of *p*-divinylbenzene, *m*-divinylbenzene, and *o*-, *m*-, and *p*-ethylvinylbenzene (EVB) [7].

For poly(styryl)lithium chains, the rate of crossover to DVB is comparable to the rate of DVB homopolymerization, and both of these rates are faster than the rate of the linking reaction of poly(styryl)lithium with the pendant double bonds in the poly(vinylstyrene) block formed from DVB. Therefore, it would be expected that the DVB block formed by crossover from poly(styryl)lithium would be relatively uniform and that the linking reaction would generally occur after the formation of the DVB block. In general, the linking effi-

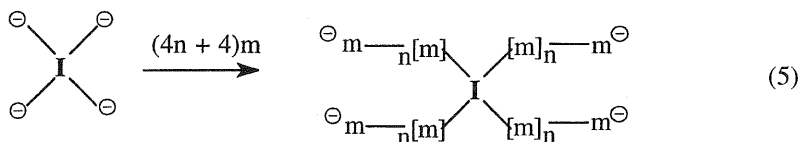
ing is reported ($\sim 92\%$) to form stars with an average arm functionality of approximately 6.

B. Multifunctional Initiators

1. General Aspects

Living polymerization using a homogeneous, multifunctional initiator of functionality n can, in principle, form a star-branched polymer with n arms (see Eq. (5) for $n = 4$) and a low degree of compositional heterogeneity among the arms if the following conditions prevail:

1. All of the initiating sites must participate in initiating chain growth (quantitative, efficient initiation). This ensures uniform and predictable arm molecular weights.
2. The rate of initiation must be rapid or competitive with respect to the rate of propagation. This is required to obtain a narrow molecular weight distribution.
3. All propagating centers must be equally reactive with respect to chain growth (addition of monomer).



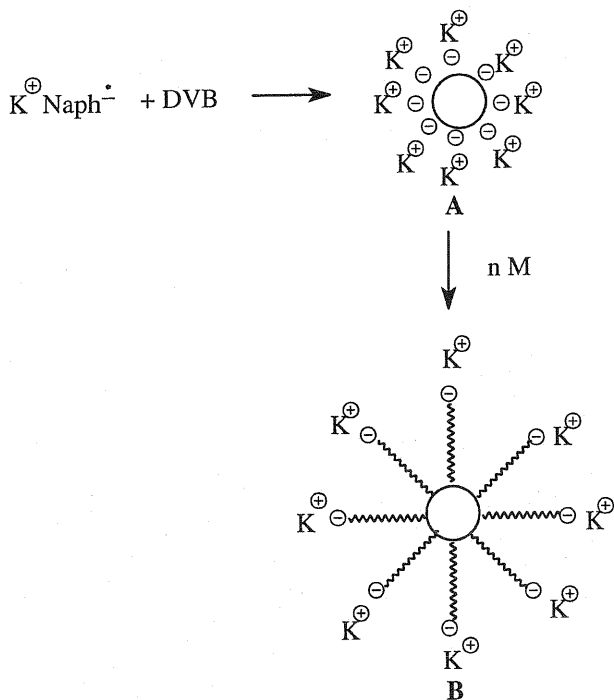
Unfortunately, few multifunctional initiators satisfy the preceding requirements. The high chain segment density in a growing star-branched molecule exacerbates complications arising from chain end/chain end interactions such as aggregation of ionic species, oxidation–reduction reactions of organo-metallic centers, and bimolecular termination reactions. As a consequence of these problems, few well-behaved multifunctional initiating systems are available.

2. Multifunctional Initiators from DVB

The ability to effect the concurrent polymerization and branching reactions of polymeric organolithium compounds with DVB [31] and form a soluble, non-gelled product was extended by Burchard and co-workers [38] to form a multifunctional initiator. DVB was first polymerized using butyllithium in benzene to form soluble microgels of high molecular weight. These microgels with their attendant anionic groups were used as multifunctional initiators to polymerize

monomers such as styrene. For example, when the ratio of $[DVB]/[BuLi]$ was 2, the microgel exhibited $M_n = 1.9 \times 10^3$ g/mol ($M_w/M_n = 16.8$) and the resulting polystyrene star had a calculated star arm functionality of 6 [3].

This method has been extended by Rempp and co-workers [39,40] as a general “core-first” method to prepare star-branched polymers, as shown in Scheme 4. The “plurifunctional” metalorganic initiator (**A**) was prepared by potassium naphthalene-initiated polymerization of DVB in tetrahydrofuran (THF) at -40°C with $[DVB]/[K^+]$ ratios of 0.5–3. Microgel formation was reported outside of this stoichiometric range or when *m*-DVB was used instead of either *p*-DVB or the commercial mixture. Within the prescribed stoichiometric ratios, star polymers (**B**) with arm functionalities varying from 8 to 42 were reported. As expected for this type of process, the polydispersities were described as being quite broad and were attributed primarily to a random distribution of core sizes and functionalities.



Scheme 4

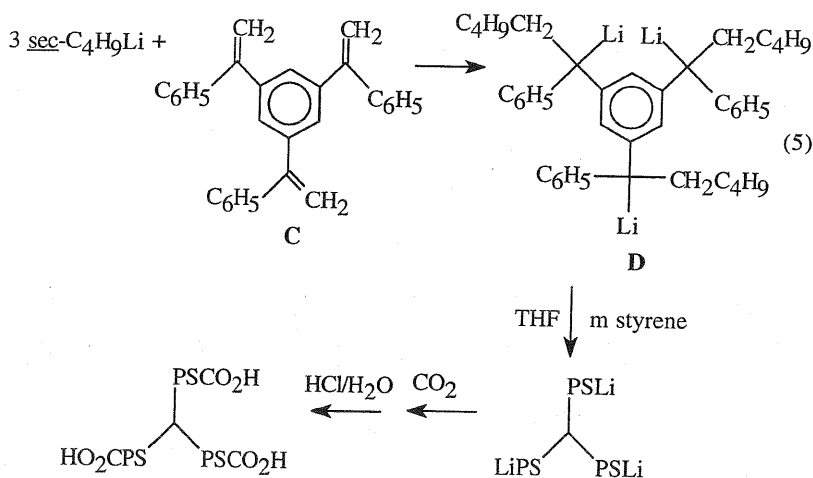
3. Trilithium Initiator Based on 1,1-Diphenylethylene

One of the few hydrocarbon-soluble, trifunctional organolithium initiators has been prepared by the reaction of 3 moles of butyllithium with a trifunctional analog of 1,1-diphenylethylene, as shown in Scheme 5 [41].

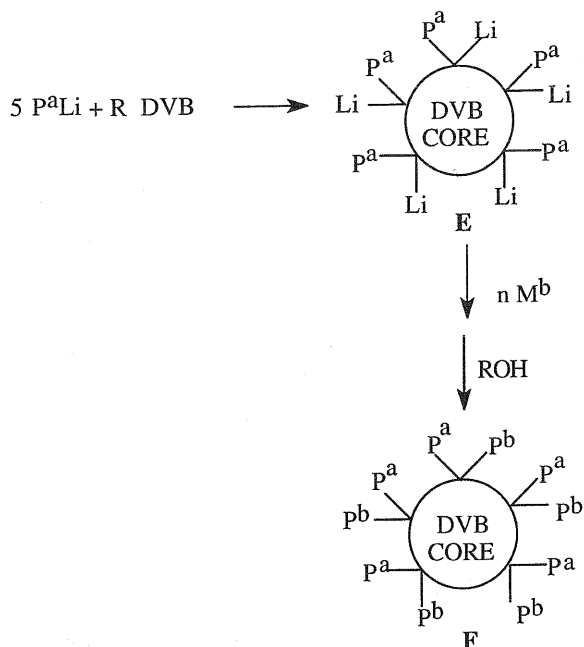
The lack of oligomerization of 1,1-diphenylethylene units provides the basis for stoichiometric additions to this precursor. In the presence of small amounts of THF ($[THF]/[BuLi] = 20$), this initiator formed well-defined, three-armed star polymers that could be quantitatively carboxylated, as shown in Scheme 5.

4. Heteroarm Star-Branched Polymers by Living Linking Reactions with DVB

Eschwey and Burchard [42] recognized that the products of the reaction of DVB with polymeric organolithium compounds are living polymers (see Schemes 2 and 3) that could function as *polyfunctional, macromolecular initiators*, as indicated in Scheme 6 for linking of five polymeric organolithium chains (P^a). This type of process has been described as a living linking reaction [43]. Thus, after DVB linking of short poly(styryl)lithium chains to form the living, linked star polymer, **E**, additional styrene or isoprene monomer (M^b) was added to double the number of arms, in principle, and form a heteroarm,



Scheme 5



Scheme 6

star-branched polymer, **F**. Preliminary viscosity and light-scattering data were consistent with heteroarm, star polymer formation. However, the difficult determination of the uniformity of the arms and the efficiency of the reinitiation reactions was not established. This “core-first” heteroarm star synthesis method based on DVB linking of poly(styryl)lithium has been applied to the synthesis of *star*-polystyrene-*star*-poly(*n*-butyl methacrylate) [44] and *star*-polystyrene-*star*-poly(*t*-butyl methacrylate) [40,45].

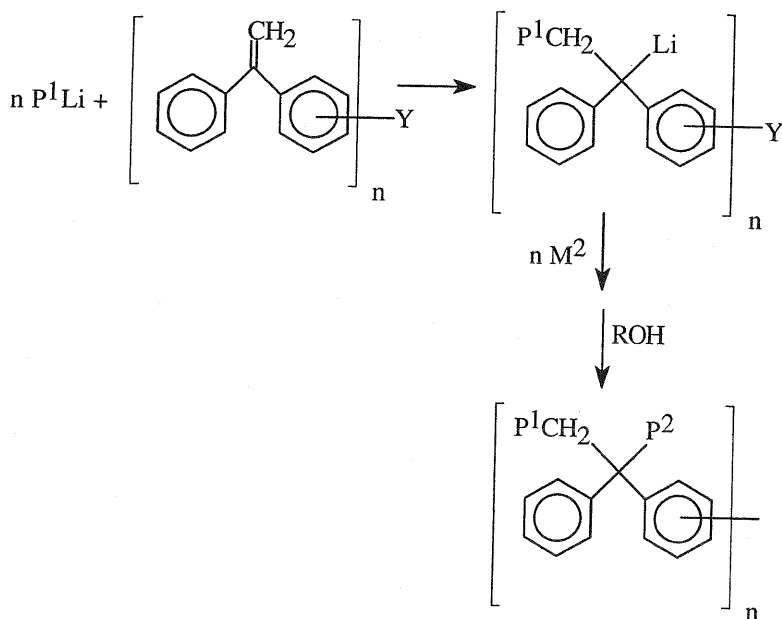
Thus, the DVB linking methodology for the synthesis of both regular star-branched polymers (see Schemes 2 and 3) and heteroarm, star-branched polymers (Scheme 6) is very versatile, efficient, and rapid; these attributes are of considerable technological importance. Unfortunately, these methods lack the precision and control necessary for the synthesis of polymers with well-defined structures and low degrees of compositional heterogeneity. However, the insight gained from these methods has led to other general methods for the synthesis of both regular star-branched polymers and heteroarm star-branched polymers. For example, ethylene glycol dimethacrylate has been used as a mul-

tifunctional linking agent for lithium poly(methyl methacrylate) to make the corresponding regular star-branched polymers [46]. By using multifunctional 1,1-diphenylethylene derivatives instead of multifunctional styrene units for addition reactions with simple and polymeric organolithiums, general methods for the synthesis of well-defined multifunctional initiators (see Scheme 5), macromonomers, as well as regular and heteroarm, star-branched polymers have been developed, as shown in Scheme 7 [9].

III. DENDRIMERS AND HYPERBRANCHED POLYMERS

In the previous sections, star-shaped polymers were discussed. In this section, highly branched oligomers or polymers, as distinct from simple star-shaped polymers, will be considered. Several excellent, recent reviews are available on this subject [10–14,47,64,65].

Dendrimers are highly branched, three-dimensional macromolecules with a branch point at each monomer unit; they have structural features that are



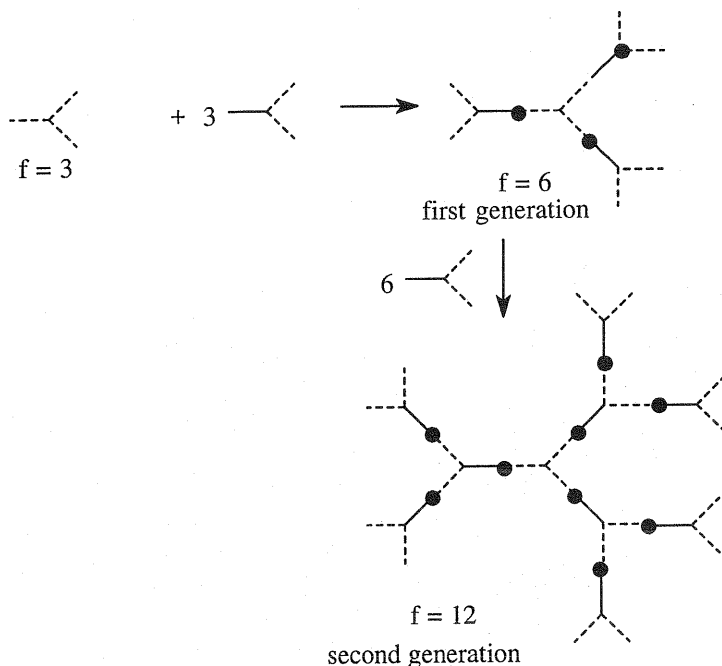
Scheme 7

analogous to the structure of trees [14]. Dendrimers have exact, monodisperse structures built layerwise in generations around a core moiety [10].

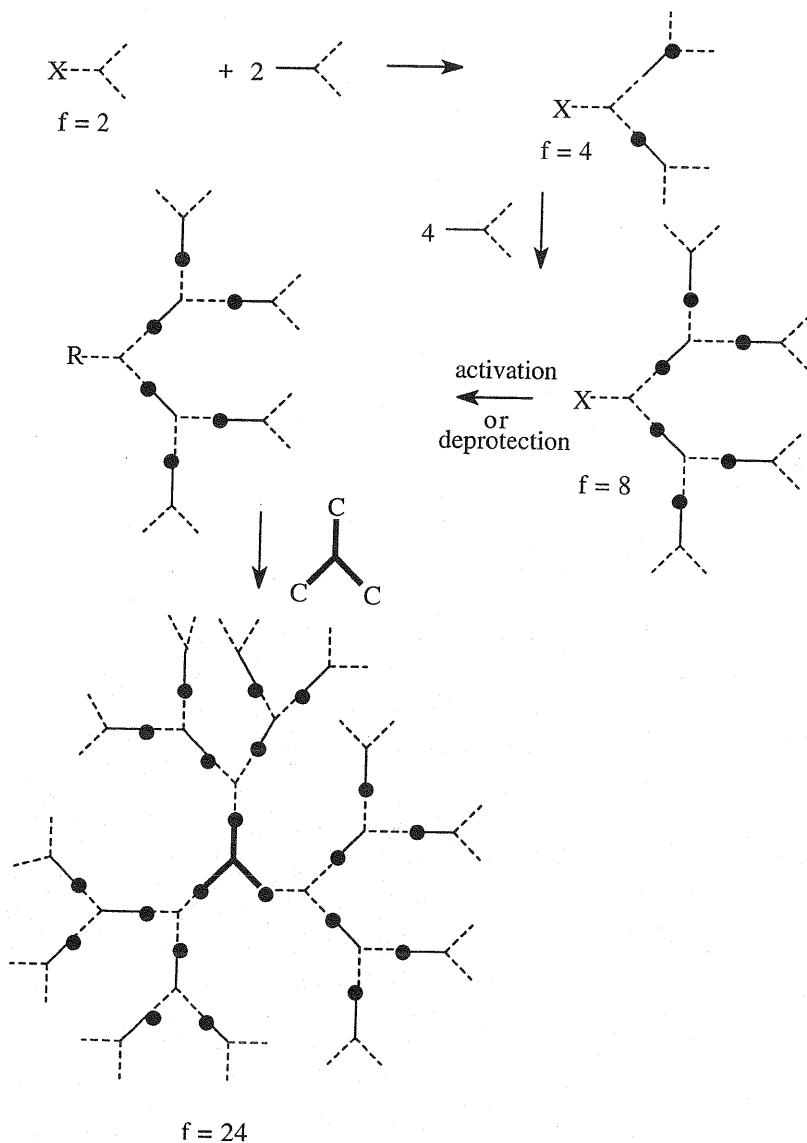
A. Synthesis of Dendrimers and Hyperbranched Polymers

1. Dendrimers

The synthesis of dendrimers generally involves numerous protection/deprotection and purification steps, but the general architectural growth patterns for the divergent and convergent routes are shown schematically in Schemes 8 and 9, respectively, where f represents the functionality of each structure, — — and ----- represent complementarily reactive functional groups, X is a latent functional group, C represents a complementary functional group, and \cdot represents a chemical bond. It is important to note that because of the complementary functionality of the dendrimers and the growth units there are no dendrimer-dendrimer reactions and the AB_2 -type units are prevented from reacting with



Scheme 8 Example of growth steps for formation of dendrimer (2 generations) by the divergent method.

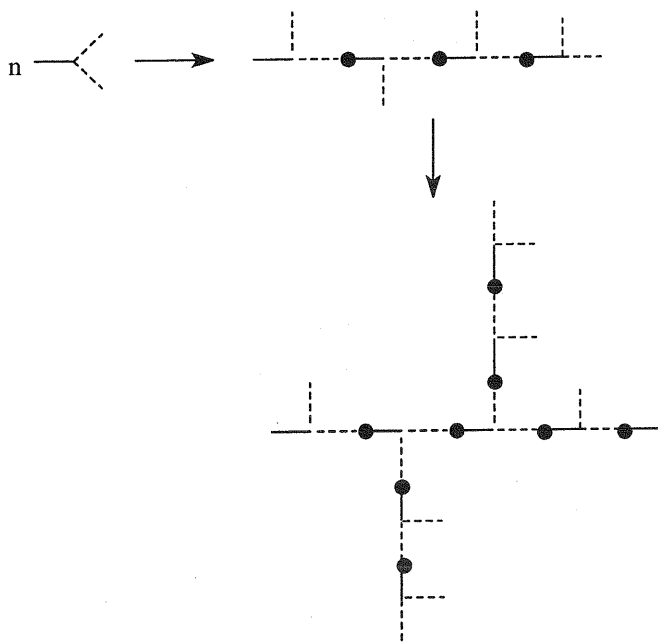


Scheme 9 Formation of dendrimer by the convergent method.

each other by suitable protecting groups on the B units. An important feature of dendrimers that is readily apparent even after the second generation is that they have high functionality and that these functional groups would be expected to be located primarily on the periphery of the dendrimers and to be accessible for chemical and physical interactions. It should be noted that the convergent synthetic route is very versatile since the final coupling step can be effected with different types of dendrons [14].

2. Hyperbranched Polymers

Hyperbranched polymers are prepared by the direct, one-step polycondensation of AB_x monomers with two different types of functional groups (A and B) that can react with each other to form a covalent bond, and the total number of reactive sites is $x + 1$ ($x \geq 2$) [48]. Hyperbranched polymers are highly branched like dendrimers, but their structure is not regular or highly symmetrical because linear segments can be formed, as shown in Scheme 10. It is important to note that in 1952 Flory [49] recognized the unique polymer structural type that



Scheme 10 Formation of hyperbranched polymers.

could be formed by self-condensation of AB_x monomers and even developed the mathematical description of molecular weight and molecular weight distribution as a function of the percentage of reaction of the functional groups. Hyperbranched polymers can be formed directly in a one-step reaction; therefore, to the extent that their properties approach those of dendrimers, they provide an expeditious and economical pathway to highly branched polymers.

3. Growth Reactions for Dendrimer Synthesis

Most dendritic polymers have been synthesized by condensation reactions. A wide variety of highly branched polymers, such as polyesters, polyamides, polyethers, polyphenylenes, polyarylacetylenes, and polycarbosilanes have been prepared by condensation mechanisms. Recently, synthetic methods to prepare polydendrons and hyperbranched polymers using vinyl monomers have been reported by several research groups [50–53]. The simplest application of vinyl polymerization involving dendrimers involves the polymerization of a vinyl monomer with an attached dendron (dendritic fragment) to form a polydendron. A schematic representation of a polydendron is shown in Figure 1b in comparison with a tridendron dendrimer (Figure 1a). The interest in the vinyl type of polydendron having dendrons (dendritic fragments) attached to the side chains comes from their potentially different topologies and properties.

Hawker and Frechet [50] prepared a dendritic macromonomer using the convergent-growth route to prepare a polyether dendron. The dendron core functional group (R in Scheme 9) was a hydroxymethyl group that was reacted with chloromethylstyrene to form the styrene-functionalized dendritic macromonomer. This macromonomer was copolymerized with styrene monomer using standard free-radical polymerization conditions.

Schluter and co-workers [51] have homopolymerized an analogous

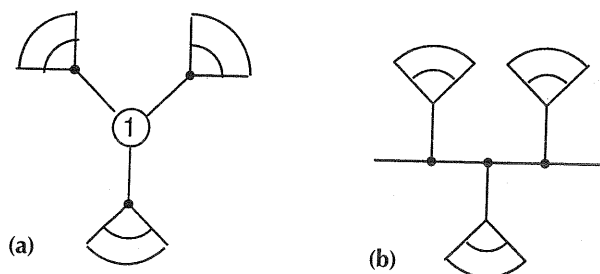


Figure 1 Comparison of the two-dimensional projections of a tridendron dendrimer (a) and a vinyl polymer (polydendron) carrying dendrons attached on the side chain (b).

series of styrene-functionalized dendritic macromonomers. For third-generation dendrons, the degrees of polymerization were 23–62. Light-scattering analysis indicated that these polymers were best described as Gaussian chains. It was concluded that the steric requirements of these side chains were insufficient to give cylindrical structures.

Xi and co-workers [52] prepared methacrylate-functionalized dendritic macromonomers by conversion of the hydroxymethyl group of the polyether dendron to the corresponding bromide and then functionalization with methacrylic acid. Free-radical polymerization of the macromonomer corresponding to a second-generation dendron resulted in formation of a relatively low molecular weight product ($X_n = 6-7$).

Schluter and co-workers [53] have also prepared a poly (*p*-phenylene) with dendritic branches by condensation polymerization. The structure of this polymer would be expected to be cylindrical because the backbone chain corresponds to a rigid rod.

A new block type of dendritic polymer has been prepared by Meijer and co-workers [54,55]. Polystyrene-*block*-dendron (PS-dendr-(COOH)*n*) was prepared by a divergent dendrimer synthetic methodology using an amine-functionalized polystyrene of well-defined structure as the core for the synthesis of a poly(propylene imine) dendrimer. A representation of the structure is shown in Figure 2. It was reported that the amphiphilic dendrimer exhibited a remarkable generation-dependent aggregation behavior in a variety of salt solutions regardless of pH.

4. *Synthesis of Hyperbranched Polymers By Self-Condensing Vinyl Polymerization*

Frechet and co-workers [56] have developed a new methodology for synthesis of hyperbranched polymers by combining both step growth polymerization and chain growth polymerization with dendrimer units formed by either the converging or diverging pathways, as illustrated in Scheme 11. The key element in this process is to use a monomer that has both a vinyl group and a pendant group that can be activated to form an initiating moiety.

B. Structure and Characterization

One of the primary differences between the star-branched polymers described previously and dendritic or hyperbranched polymers is their chain segment density distribution. For star-branched polymers, the chain segment density is highest at the core and decreases as the distance from the core increases. In contrast, for dendritic and hyperbranched polymers the chain segment density increases as the distance from the core increases (with increasing generations

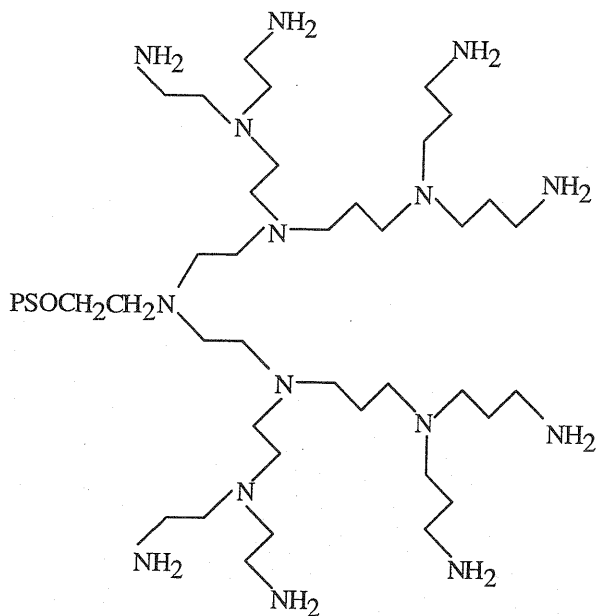


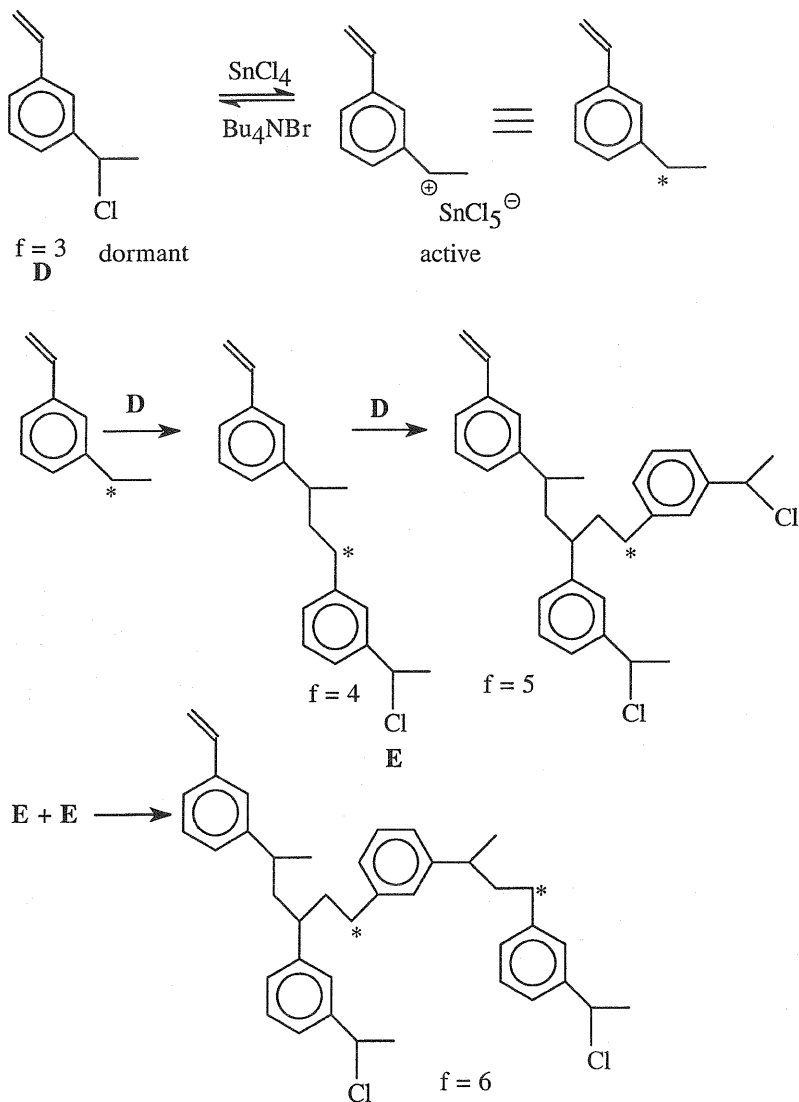
Figure 2 Structure of Ps-dendr-(NH₂)₈.

for dendritic polymers) [10]. In fact, it is calculated that a maximum number of dendrimer generations can be formed (starburst dense-packed generation), beyond which only defect structures can be generated [10,57].

We have discussed the synthetic methods for dendrimers and hyperbranched polymers. As shown in Schemes 8, 9 and 10, the molecular architecture of dendrimers and hyperbranched polymers will be remarkably affected by the core and its functionality, the branching-site multiplicity, the chain length depicted as a shell surrounding the central core, and so on. The size and the physical properties of the formed polydendrons will be greatly affected by these variables. Among these variables, the most important factor is the degree of branching (DB) represented in Eq. (6), as defined by Frechet and co-workers [58], which is directly related to polydendron size (hyperbranched polymer).

$$DB = \frac{\sum \text{dendritic unit} + \sum \text{terminal unit}}{\sum \text{dendritic unit} + \sum \text{terminal unit} + \sum \text{linear unit}} \quad (6)$$

A variety of methods have been used to characterize the structures of dendrimers. In contrast to common polymers, which are polydisperse, dendrimers can be obtained as truly monodisperse materials as shown by mass



Scheme 11 Hyperbranched polymers by self-condensing vinyl polymerization.

spectrometry [14]. The degree of branching for a perfect dendrimer is 1.0 (100%). In contrast, hyperbranched polymers exhibit DB values in the range between 0 and 1 (0.4–0.7 for polyesters) and broad molecular weight distributions (e.g., $M_w/M_n = 2$ –10 for polyesters) [13]. The molar mass can be investigated by low-angle laser light scattering, mass spectrometry, and size exclusion chromatography/universal calibration [13,14]. The structural perfection of dendrimers can be investigated by ^1H and ^{13}C NMR spectroscopy, electrospray ionization mass spectrometry, and matrix-assisted laser desorption/ionization mass spectrometry (MALDI). For example, the degree of branching can be investigated by NMR spectroscopy since the different units [see Eq. (6)] generally possess different chemical shifts because of the highly ordered and symmetrical branching sequence [14]. Shape-related properties can be characterized by light scattering, intrinsic viscosity measurements, and size exclusion chromatography.

The glass transition temperatures of aromatic polyesters were reported to be totally independent of the variation of the architecture or shape by comparison of dendrimer, hyperbranched, and linear analogs [59]. The thermogravimetric behavior was also found to be independent of architecture [59]. However, the glass transition temperatures of hyperbranched polyesters are very strongly dependent on the nature of the terminal groups, as is their solubility [59,60]. Thus, the solubility and thermal properties of dendrimers and hyperbranched polymers can be varied by varying the chain end groups.

C. Properties

Dendritic polymers exhibit very different properties compared with their linear analogs. For instance, they exhibit extremely high solubility in various organic solvents and low intrinsic viscosity in comparison to their linear analogs. These differences are probably a reflection of the large number of chain end functional groups as well as the influence of architectural differences [59].

Dendrimers do not exhibit linear Mark–Houwink plots [13]. The intrinsic viscosity increases with size and then decreases after about generation 4.

Many physical properties of hyperbranched aromatic polyesters, such as high solubility and low viscosity, resemble those of dendrimers. However, in contrast to dendrimers, hyperbranched polymers do exhibit a linear dependence of intrinsic viscosity on molecular weight with very low Mark–Houwink constants (0.3–0.4) [13]. In addition, their lack of reactivity toward catalytic hydrogenolysis greatly differs from that of the corresponding dendrimers, which are cleanly deprotected under mild conditions; rather their reactivity more resembles that of the corresponding linear polymers [59]. As shown in

Eq. (6), a hyperbranched polymer will resemble a dendrimer with increasing degree of branching. However, many questions still remain regarding the chemical and physical properties of hyperbranched polymers and dendrimers.

D. Applications

The synthesis, characterization, and applications of dendritic and hyperbranched polymers is an exciting active area of investigation. The “one-pot” synthesis of hyperbranched polymers suggests that their commercial exploitation will outpace that of dendrimers for many applications.

Hyperbranched polymers can be used as additives to conventional polymers, in blends, as thermosets, and as thermoplastics. In blends, it would be expected that miscibility could be varied by modification of end groups. It is considered that their addition to thermosets, blends, and additives would be expected to enhance mechanical properties and exhibit beneficial processing characteristics because of their nonentangled nature [13]. Thus, as an additive, a hyperbranched polyphenylene has been shown to reduce melt viscosity for polystyrene processing [48,61]. The processing characteristics and high functionality of hyperbranched polymers have been shown to impart desirable processing and curing characteristics to thermosets [62,63].

Investigation of the possible applications of dendrimers has been limited by their lack of ready availability [14]. It is anticipated that dendrimers may be used as a polymeric matrix for catalysts, as a membrane for gas separation, and as part of the diagnostic kit for MRI since many groups can be added to the core or to the periphery. The unique structure and solubility characteristics of dendrimers suggest that their use as dendritic micelles may be important. In addition, they may form interesting and useful monolayers [14].

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