

# Controlling the Growth of Polymer Trees: Concepts and Perspectives For Hyperbranched Polymers

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**Abstract:** This article summarizes basic principles and recent progress in the field of cascade-branched polymers. Methods for the preparation of macromolecules with hyperbranched structures are presented and compared concerning the extent of control over molecular weights and polydispersity. Step-growth and recently developed chain-growth strategies as well as enzyme and transition metal catalyzed polymerizations are discussed with respect to mechanism and future potential.

**Keywords:** dendrimers • hyperbranched polymers • nanostructures • polymerizations • polymers

## Introduction

Recently, there has been a surge of interest in globular, highly branched macromolecules. Polymers with a branch-on-branch structure are generally known as “cascade-branched” or “dendritic”. From a topological viewpoint, branch-on-branch structures are characterized by the peculiarity that there is no connecting line between any two end groups that passes *all* branching points.<sup>[1]</sup> The perfectly branched dendrimers represent the stepwise “organic” approach to branch-on-branch (i.e., treelike) structures, resulting in monodisperse polymers of unprecedented structural precision.<sup>[2]</sup> However, these highly symmetric structures can only be realized by a tedious multistep protocol, which represents their major drawback.

The polymer approaches to macromolecules with a treelike structure are based on one synthetic step only. However, this leads to a randomly branched topology, that is, branching is not achieved for every monomer unit incorporated and additional linear units are present. This type of polymer structure has already been known since the 1930s from polysaccharides such as glycogen, dextran, and amylopectin.<sup>[3]</sup>

In the early 1950s, Flory published his clear-sighted theoretical work on the so-called “random  $AB_m$  polycondensates”,<sup>[4]</sup> synthetic polymers that are prepared by the step-growth polymerization of  $AB_m$  monomers. Such monomers possess one A functionality and  $m$  complementary B groups. The only reaction in the system is the coupling of A and B groups. Most monomers used to date are of the  $AB_2$  type ( $m = 2$ ). A typical branched polymer structure obtained from an  $AB_2$  type monomer is shown schematically in Figure 1.

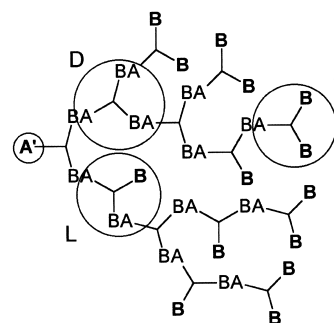


Figure 1. Schematic structure of a hyperbranched polymer based on  $AB_2$  monomer units. The three different possible incorporation modes [dendritic (D), linear (L), terminal (T)] are circled. The focal unit  $A'$  represents either one unreacted A group or can be attached to a  $B_f$  core molecule (i.e., initiator in polymerization).

In recent years, profiting from the fascination created by the structurally perfect dendrimers, such randomly branched macromolecules have been rediscovered (Figure 2) and are generally designated “hyperbranched polymers”.<sup>[5]</sup> The hyperbranched structure results in characteristic properties that strongly depend on the degree of branching: i) a globular, relatively compact shape and, consequently, ii) absence of entanglements, in pronounced contrast to linear polymer chains. These structural peculiarities usually lead to amorphous materials, since branching prevents crystallization. Furthermore, low viscosity in bulk and solution is observed. Owing to the lack of chain entanglements that act as physical cross-links in linear polymers, hyperbranched polymers are usually not very tough materials. Their appearance only depends on the glass transition temperature ( $T_g$ ), that is, high values of  $T_g$  result in brittle materials and low values in oils.

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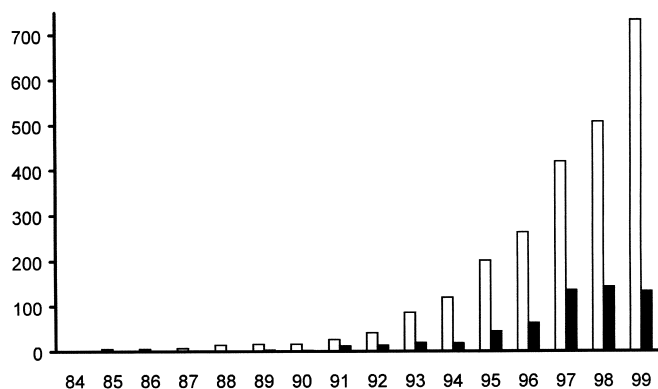


Figure 2. Number of publications on the fields of dendrimers and hyperbranched polymers since 1984 [□ dendrimers; ■ hyperbranched polymers (without polyethylenimine and branched polysaccharides)].

Numerous applications are discussed for dendrimers at present that may eventually be realized with well-defined hyperbranched polymers. The low viscosity in combination with the high functionality may be exploited for functional cross-linkers, additives,<sup>[6]</sup> and rheology modifiers,<sup>[7]</sup> as well as components in adhesives, advanced coatings,<sup>[8]</sup> structured hydrogels,<sup>[9]</sup> and novel dental composites. Furthermore, hyperbranched polymers might also be of interest in nanotechnology, for example, as building blocks for nanoscale reaction compartments,<sup>[10]</sup> as templates for nanoporous materials with low dielectric constants, or for the fabrication of defined hybrid particles (e.g., by biomineralization techniques). Other fields considered are biochemistry and biomedicine, where such macromolecules could be employed as carriers, either highly loaded for diagnostic purposes (e.g., for magnetic resonance imaging (MRI) of blood vessels)<sup>[11]</sup> or as host compartments for controlled drug-release.<sup>[12]</sup> Finally, the use as homogeneous supports for recyclable catalysts as well as for supported organic and biochemical syntheses has been suggested.<sup>[13]</sup>

Since there are numerous advanced applications for hyperbranched polymers, it is an important challenge to understand and control both the branching pattern and molecular weights as well as polydispersity. In this brief review, recent progress towards the preparation of well-defined treelike polymers is summarized. It takes into account well-known natural cascade-branched polysaccharide structures, the transition metal catalyzed polymerization of olefins, the classic  $AB_m$ -polycondensation approach, and recently developed chain-growth type polymerization mechanisms. A strict definition of the term “hyperbranched” will be used that is based on the polymerization of  $AB_m$  or latent  $AB_m$ -type monomers and a branch-on-branch structure.<sup>[1]</sup> Most systems reported to date rely on  $AB_2$  type monomers. Therefore, we will restrict our considerations to a branching multiplicity of  $m = 2$ .

### Branched Polysaccharides

Energy storage biopolymers based on  $\alpha$ -D-glucopyranose are the longest known and, in fact, most investigated hyperbranched polymers.<sup>[3]</sup> The three polysaccharides glycogen

(weight-average molecular weight ( $M_w$ ) up to  $9 \times 10^6$ , degree of branching (DB) < 16 %),<sup>[14]</sup> dextran ( $M_w$  up to  $2 \times 10^6$ , DB < 60 %), and amylopectin ( $M_w$  up to  $70 \times 10^6$ , DB < 5 %) were identified as branched macromolecules by Staudinger in the late 1930s.<sup>[15]</sup> In 1940 Meyer and Bernfeld proposed the first hyperbranched polymer model for polysaccharides.<sup>[16]</sup> Glycogen and amylopectin both consist mainly of linear (1  $\rightarrow$  4)- $\alpha$ -D linkages. These linear chains possess additional (1  $\rightarrow$  6)- $\alpha$ -D linkages at the dendritic units. Dextrans are constructed in an opposite way, that (1  $\rightarrow$  6) connections connect the linear units and (1  $\rightarrow$  3) linkages with additional (1  $\rightarrow$  2) and (1  $\rightarrow$  4) linkages represent branching points. Biosynthesis of the linear segments is controlled by specific synthetases, that is, successive propagation from the reducing end, by using activated glucose as monomer units. In contrast to synthetic branched polymers, the formation of a branching point, controlled by branching enzymes, is apparently realized by cleavage of a linear chain segment and subsequent transfer of the residue to a 6-position (3-position for dextrans) of the remaining chain.

Glycogen and dextran possess branching points randomly distributed over the molecule due to the highly dynamic polymerization/depolymerization equilibrium. Amylopectin differs significantly from glycogen, since it possesses a highly ordered microstructure.<sup>[17]</sup> Branching units are found in clusters in which on average every second unit is branched. From these clusters 1–2 cluster-connecting linear segments and 3–4 linear segments with terminal ends originate.<sup>[18]</sup> The resulting multi-cascade structure is responsible for the formation of amorphous domains from the branching clusters. The linear segments form double helices, resulting in crystallization in the course of the biosynthesis. An onionlike structure of starch granules is finally obtained as a native supramolecular structure<sup>[19]</sup>.

In summary, hyperbranching represents a natural principle for energy storage in compact macromolecules. In a somewhat simplified picture, the presence of numerous chain ends permits fast release of large quantities of glucose. The enzymatic three-step mechanism in the biosynthesis of these compounds (linear propagation, chain cleavage, chain-fragment transfer) permits precise control over the microstructure. Hence, peculiar properties, such as partial crystallization within the same hyperbranched molecule can be realized. This is still unrivaled by the synthetic approaches discussed in the following paragraphs.

### Hyperbranched Polyolefins

Simple monomers for the preparation of branched polymer structures are olefins like ethylene and propylene. In recent reports branched polyolefins obtained from these monomers with Ni-, Pd-, Ta-, and also Ti-based catalysts have been mentioned as being “hyperbranched”.<sup>[20]</sup> However, the term should be handled with caution in this context, since the stringent structural criterion, the presence of extensive branch-on-branch structures is not fulfilled in most cases and is difficult to prove. When ethylene is polymerized with Ziegler type catalysts based upon early transition metals

(most commonly Ti/Al systems), linear polyethylene is obtained. Branched topologies are either prepared by the uncontrolled high-pressure free-radical polymerization of ethylene (low density polyethylene, LDPE) or by controlled copolymerization of ethylene with higher 1-olefins (e.g., 1-hexene) in the presence of “single site” catalysts, resulting in linear low density polyethylene (LLDPE).<sup>[21]</sup> However, the latter syntheses commonly do not yield branch-on-branch architectures, but linear polyethylene with various side chains.

Recently, a new approach has been developed, based on late transition metal complexes (i.e., Ni and Pd) to produce highly branched polyethylene in the absence of a comonomer. In 1985 Fink et al. reported the 2, $\omega$ -polymerization of 1-pentene in the presence of bis(1,5-cyclooctadiene)nickel and aminophosphorane as cocatalyst, in which the 1-olefin was not inserted in the usual 1,2-manner.<sup>[22]</sup> Instead of the expected polyethylene with propyl side chains a polyethylene with methyl branches was obtained, which can formally be described as an alternating copolymer of ethylene and propylene. In general, the segment length between alkyl branches was controlled by the length of the 1-olefin. During the 1990s Brookhart et al. developed Ni and Pd catalysts with diazadiene ligand framework that lead to the formation of highly branched polyethylenes in the polymerization of ethylene. This is explained by the migration/insertion mechanism of the polymerization (“chain walking”).<sup>[23]</sup> After an insertion step of a monomer, the transition metal is able to “walk” back along the polyethylene chain, permitting not only growth at the chain end but also at any point of the chain reached during migration (Figure 3).

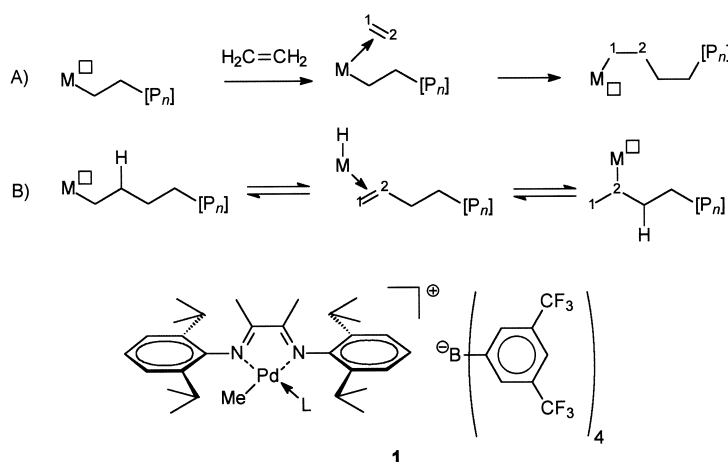


Figure 3. Polymerization of ethylene by late transition metal catalysts (e.g., **1**). A) Propagation by 1,2-insertion. B) Catalyst migration by  $\beta$ -H-elimination and 2,1-reinsertion; L = NCR, OEt<sub>2</sub>.

As illustrated in Figure 3A, the transition metal inserts ethylene in a 1,2-manner. In contrast to other “single site” catalysts, late transition metal catalysts undergo reversible  $\beta$ -H-elimination (Figure 3B). The subsequent 2,1-reinsertion of the vinyl-terminated polymer chain into the metal–hydrogen bond leads to the formation of a methyl branch upon further propagation at the new metal position. When the metal migrates further by this mechanism (Figure 3B), longer alkyl branches are formed upon propagation (Figure 3A).

Brookhart et al. reported the synthesis of highly branched polyethylenes by the use of MAO-activated nickel diimine complexes and palladium diimine complexes with bulky counter ions **1**.<sup>[23c–e]</sup> The amorphous polymers, prepared by Pd catalysis, possess approximately 100 branching points (tertiary carbons) per 1000 carbon atoms, independent of pressure and temperature.<sup>[24]</sup> In contrast, for Ni catalysts high ethylene pressure leads to linear short-chain branched polymers, while low pressure favors the formation of longer side-chains, that is, at low ethylene pressure “chain walking” can compete with propagation (Figure 3). In other words, the catalyst has enough time to walk along the chain before inserting the next monomer unit, which leads to a large number of longer branches. The most important question in the context of hyperbranched polymers is whether branch-on-branch topologies are possible by this mechanism. This requires, in accordance with the mechanism in Figure 3, the catalyst has to “walk” across a tertiary carbon. The simplest branch-on-branch structure in such polyethylenes is a *sec*-butyl branch, which in fact could be detected by <sup>13</sup>C NMR spectroscopy.<sup>[25]</sup> It has to be emphasized that precise structural characterization of the branched polyethylenes represents a major problem. In contrast to the hyperbranched structures discussed in the ensuing paragraphs, NMR spectroscopy can only lend limited support to a cascade-branched topology owing to the complexity of the spectra and the comparatively low branching density (<10 *sec*-butyl branches per 1000 carbon atoms). Thus, structural evidence for cascade-branching has to be obtained from other methods. In recent work, McLain et al. used combined light-scattering and intrinsic viscosimetry experiments that, on the basis of the compact polymer structures observed in solution, appear to support the postulated chain-walking mechanism in palladium-diimine catalysis **1** at low ethylene pressures.<sup>[26]</sup> In contrast to all other hyperbranched structures, these branched polyethylenes represent purely aliphatic hydrocarbons. Incorporation of functional monomers in order to achieve polyfunctionality as in the case of “typical” AB<sub>2</sub> systems represents an additional and worthwhile challenge in the future.<sup>[23d,e, 25]</sup>

## Polycondensation and Polyaddition of AB<sub>2</sub> Monomers

Based on the ingenious work of Flory,<sup>[4]</sup> the common synthetic approach to hyperbranched polymers is polymerization of AB<sub>2</sub> (or AB<sub>m</sub>) monomers possessing complementary A and B functionalities (e.g., hydroxyl and carboxylic acid groups **7**). It is a typical feature of step-growth reactions of this type that each polyfunctional oligomer present in the reaction mixture may couple with any other species in the absence of cross-linking.<sup>[27]</sup> Over the past 15 years more than 150 new AB<sub>2</sub> type monomers have been reported, leading to, for example, polyphenylenes **2** (Suzuki-coupling)<sup>[5]</sup>, poly(phenylacetylenes) **3** (Heck-reaction)<sup>[28]</sup>, polycarbosilanes and polycarbosiloxanes **4** (hydrosilylation)<sup>[29]</sup>, poly(ether ketones) **5** (nucleophilic aromatic substitution)<sup>[30]</sup> and polyesters **6**, **7** (condensation)<sup>[8, 31]</sup> (Figure 4). As a consequence of the polycondensation or polyaddition kinetics, high degrees of polymerizations

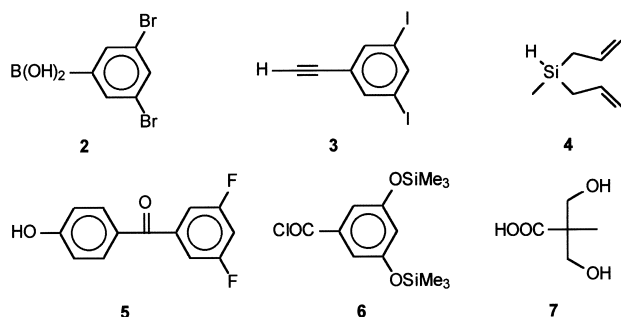


Figure 4. Examples of AB<sub>2</sub> monomers leading to hyperbranched polyphenylenes and poly(phenylacetylenes) (2, 3), polycarbosilanes (4), poly(ether ketones) (5), and polyesters (6, 7).

(DP<sub>n</sub>) are only achieved at high conversion (modified Carothers' equation). The polydispersity ratio ( $M_w/M_n$ ) is expected to be in the range of DP<sub>n</sub>/2 or DP<sub>w</sub><sup>1/2</sup>,<sup>[1, 4]</sup> and is thus extremely large.<sup>[32]</sup> In addition, intramolecular cyclization of the growing macromolecules is possible and highly probable through the reaction of the single focal A' group with a B group of the same molecule (Figure 1, cf. Figure 6B below). This undesired reaction further complicates these polymerizations and limits molecular weights drastically.<sup>[33]</sup> Monomers with cyclic B groups (e.g., oxazolines<sup>[34]</sup>) that react in the presence of a catalyst do not lead to a different result, since the basic kinetic features of the polymerization are unchanged.

In summary, AB<sub>2</sub> batch polycondensation permits no control over the polymerization reaction, because of the restrictions related to the complementary nature of the functional groups A and B and the resulting limitations concerning molecular weight and polydispersity.

Recently, it has been proposed that batch copolymerization of a core molecule with *f* functional groups (B<sub>*f*</sub>) might lead to an improved control of polycondensation reactions through the AB<sub>2</sub>-monomer/B<sub>*f*</sub>-core ratio employed.<sup>[35]</sup> In this case monomer 7 was added in portions, which represents the theoretical generations of a structurally perfect dendrimer. However, if this strategy is applied, attachment to these B<sub>*f*</sub> cores competes with cyclization (i.e., intramolecular reaction of the A' group with a B group of the same molecule), when flexible monomers are used. This leads to a loss of control over molecular weights.<sup>[33d]</sup> Nevertheless, for monomers of a size sufficient to render cyclization improbable, the concept of portionwise addition may possess valuable potential, as shown by Möller et al. in recent work, by using methyldiundecenylsilane in a hydrosilation polyaddition reaction.<sup>[36]</sup> In this case, a pronounced molecular weight increase with added monomer portions was observed.

### Polymerization of Latent AB<sub>2</sub> Monomers

In 1994, Fréchet et al. introduced the self-condensing vinyl polymerization (SCVP) as an alternative concept to the AB<sub>2</sub> polycondensation.<sup>[37]</sup> SCVP is based on a vinyl monomer that additionally bears an initiating group (8) (*inimer* = initiator + monomer). Hence, these monomers allow two modes of

propagation: i) polymerization of the double bond (=chain growth) and ii) condensation of the initiating group with the double bond (=step growth). This class of monomers can be considered as *latent* AB<sub>2</sub> monomers, since the second B functionality is only released upon reaction of the A group (Figure 5). In perfect analogy to SCVP, heterocyclic monomers with a pending B functionality (9) represent a second

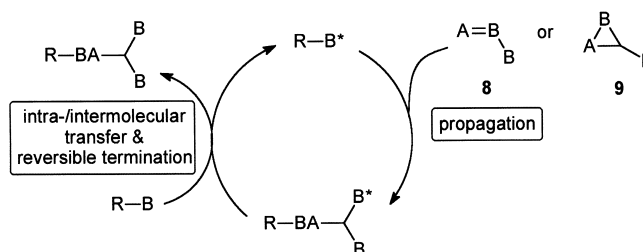


Figure 5. Polymerization of latent AB<sub>2</sub> monomers with reversible activation of B-groups (B → B\*). Monomers can be either of vinylic (8) or cyclic structure (9).

class of latent AB<sub>2</sub> monomers (polymerization by ring-opening = chain growth, condensation of the pending B group with the heterocycle = step growth). Hyperbranched polymers obtained from such self-condensing ring-opening polymerizations (SCROP) have been known for a long time (Figure 7 below). This mechanism is operative in the polymerization of aziridine 10 (which leads to hyperbranched polyethylenimine)<sup>[38]</sup> and glycidol 11 (leading to polyglycerols).<sup>[39]</sup> Recently, other cyclic monomers representing latent AB<sub>2</sub> structures have been developed, including hydroxy-oxetanes 12<sup>[40]</sup> and hydroxycaprolactones 13 (Figure 7).<sup>[41]</sup>

The general principle of the polymerization of latent AB<sub>2</sub> monomers is illustrated in Figure 5. Propagation always proceeds by attack of an activated B group on the double bond (SCVP) or the heterocycle (SCROP, A group). This activates the latent B group, while the pending B group remains inactive. The major prerequisite of the polymerization mechanism to obtain a multibranching polymerization is the reversible termination step, that is, by intra- and intermolecular transfer of the active propagation site all B groups present in the system can become active. This transfer has to be very efficient, since the number of potential propagation sites (*dormant* sites) on the polymer increases with increasing degree of polymerization. In vinyl systems (SCVP) cationic 14,<sup>[37]</sup> controlled radical (i.e., group transfer polymerization (GTP),<sup>[42]</sup> atom transfer radical polymerizations (ATRP, 15),<sup>[43]</sup> and coordinative catalysis<sup>[44]</sup> have been employed. For cyclic monomers (SCROP), polymerizations rely on anionic (11),<sup>[39b,e]</sup> cationic (10,<sup>[38]</sup> 11,<sup>[39d,e]</sup> and 12<sup>[40]</sup>), and metal-mediated mechanisms (13).<sup>[41]</sup> The major advantage of these latent AB<sub>2</sub> monomers compared with "classic" AB<sub>2</sub> monomers is their high reactivity upon activation of the latent B group, since commonly the propagation is based on efficient, well-known polymerization reactions. However, if exclusive chain-growth without transfer occurs, only linear functional polymers are obtained from latent AB<sub>2</sub> monomers.<sup>[45]</sup>

The general drawback of the random polymerization of latent  $AB_2$  monomers lies in the fact that self-condensing steps are still present in the polymerization. In other words, these monomers are still able to autopolymerize in a non-initiated and, thus, uncontrolled fashion; this results in the formation of cyclic species, as it is illustrated for cyclic latent  $AB_2$  monomers in Figure 6. In the first step the active

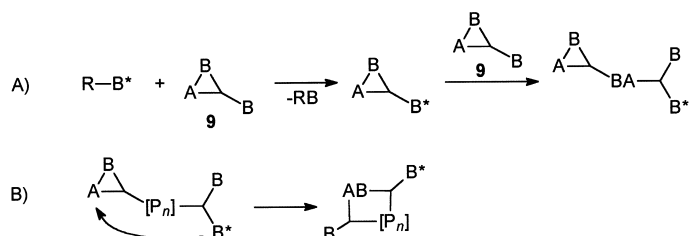


Figure 6. A) Self-condensing of latent cyclic  $AB_2$  monomers **9** leading to the formation of undesired polymerizable oligomers. B) Cyclization of polymerizable oligomers by intramolecular reaction.

propagation site is transferred to the non-latent B group of a monomer, enabling it to propagate. In this manner oligomers with a polymerizable core unit are formed. Both the reaction of these species with another polymer molecule and intramolecular cyclization lead to a broad molecular weight distribution similar to “classic”  $AB_2$  polycondensations.<sup>[46]</sup> Since intramolecular cyclization can occur at any time of the polymerization, no control of the reaction is achieved.

### Polymerization of Bilatent $AB_2$ Monomers

Extending the concept of latent monomers, systems would be desirable in which both B groups are *only* activated upon attachment of the A group to the growing polymer. In this case, the monomer can only polymerize by way of an initiated chain-growth process, and step-growth is impossible. As a consequence, an initiator with free B groups ( $B_f$ ) has to be employed in addition to the catalyst, guaranteeing activity of all propagation sites. Since propagation exclusively proceeds by a chain-growth type of mechanism, such monomers do not exhibit cyclization as a side reaction (cf. Figure 6). Thus, control of molecular weight is achieved simply by the monomer/initiator ratio in analogy to common, controlled linear polymerization systems. In very elegant work, Suzuki et al. in 1992 published the first example of this type of cyclic monomer, followed by a second example six years later.<sup>[47]</sup> These systems are based on cyclic carbamates **16** and **17**, which bear a double bond in  $\alpha$ -position to the oxygen atom

(Figure 7). Upon Pd-catalyzed activation of the allyl functionality, an amine can react with the heterocycle under extrusion of  $CO_2$ , resulting in the liberation of a primary amine that is equivalent to two B groups. Since the heterocycle is opened only by primary and secondary amines but not by the carbamate itself, the multibranching polymerization occurs in the absence of side reactions and unprecedentedly narrow polydispersities ( $M_w/M_n = 1.2–1.4$ ) were obtained. We propose to designate such monomers “bilatent” in order to distinguish them from the above-mentioned monomers with only one latent B group.

### Pseudo Chain-Growth by Slow Monomer Addition

Although the use of bilatent  $AB_2$  monomers permits very efficient control in multibranching polymerizations, this approach is restricted to peculiar monomers that are to date only accessible by multistep syntheses. It has been shown by recent theoretical work, that  $AB_2$  monomers, and especially latent  $AB_2$  monomers, can be polymerized in a controlled manner, when the polymerization is carried out under slow-monomer-addition conditions (indicated by the arrow in Figure 7).<sup>[48]</sup> This concept is based on two general principles: i) the monomer is continuously and slowly added to the active polymerization mixture and ii) an  $f$ -functional initiator  $B_f$  is used. This strategy results in a very low monomer concentration actually present in the reaction mixture and, therefore, exclusive reaction of the monomer with the growing polyfunctional macromolecules. Ideal slow monomer addition implies that conversion of the A groups is 100% at all times, that is, before new monomer is added, the previously added portion has to be consumed. In the ideal case, this results in chain-growth-like conditions and renders it possible to prepare hyperbranched polymers in a process that resembles an initiated chain-growth polymerization. This concept, first applied to the  $AB_2$  monomer **6**,<sup>[49]</sup> recently permitted the first controlled synthesis of a hyperbranched polymer based on the base-catalyzed ring-opening multibranching polymerization

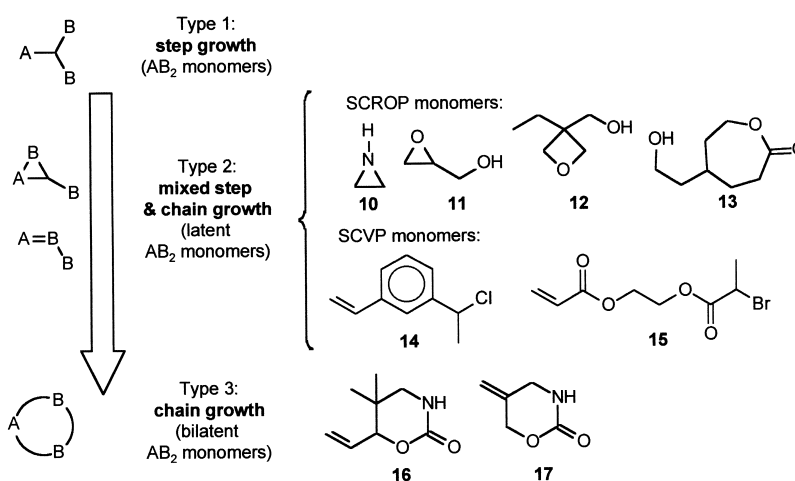


Figure 7. Classification of different types of  $AB_2$  monomers by polymerization mechanism (SCROP: self-condensing ring-opening polymerization, SCVP: self-condensing vinyl-polymerization). Arrow indicates increasing control of the reaction due to increasing chain-growth character.

of glycidol **11** (latent AB<sub>2</sub> monomer).<sup>[50]</sup> Similarly, slow monomer addition conditions permitted the controlled synthesis of hyperbranched poly(phenylacetylene)s based on monomer **3**.<sup>[28, 51]</sup> In both cases, materials with low polydispersity were obtained.

### Degree of Branching

The previous sections of this short summary have been directed at the control of molecular weights and strategies to lower the polydispersity in multibranching polymerizations. In this final paragraph, we will briefly discuss possibilities to control the extent of branching in the respective hyperbranched polymers. The experimental parameter commonly used in this context to characterize the extent of hyperbranching is the degree of branching DB. However, for historic reasons and related to the respective analytical methods employed, different parameters are currently in use to describe the extent of branching in branched polysaccharides, polyolefins, and hyperbranched polymers. This complicates the comparison of the different classes of cascade-branched polymers with respect to the achievable branching density. In the case of polysaccharides, the extent of branching is usually given in terms of branched monomer units per total number of monomer units, whereas in the polyolefin community branching is measured in branched carbons per 1000 carbon atoms.<sup>[52]</sup> For common hyperbranched polymers obtained from AB<sub>2</sub> monomers, the degree of branching (DB) is employed. The DB describes the relative perfection of a branch-on-branch structure compared with the analogous, structurally perfect dendrimer, which possesses a DB of 100% by definition; linear polymers possess a DB of 0%<sup>[31, 53]</sup>. In an ideal random polymerization of AB<sub>2</sub> monomers, the ratio of dendritic (D), linear (L) and terminal (T) units (cf. Figure 1, commonly determined from NMR spectra) is expected to be 1:2:1, which corresponds to a DB of 50%.<sup>[53]</sup> This maximum value achievable is independent of whether an AB<sub>2</sub>, a latent AB<sub>2</sub>,<sup>[53]</sup> or a bilatent AB<sub>2</sub> monomer<sup>[47]</sup> is used. Lower DBs can be realized by copolymerization of an AB<sub>2</sub> with a linear AB monomer.<sup>[55]</sup> The pseudo-chain growth type of kinetics under slow-monomer-addition conditions affects the statistics of the branching reaction. It has been predicted theoretically that under ideal conditions the probability of the formation of linear units is only half of that in a common bulk polymerization (abundance of D, L, and T units = 1:1:1), leading to a maximum DB of 67%.<sup>[48]</sup> Experimental results confirm this prediction; however, steric factors and reactivity differences lead to values between 50% and 67%.<sup>[49, 50]</sup> A further increase of DB towards 100% (i.e., absence of linear units) can only be achieved by the use of peculiar monomers (exhibiting a strong preference towards the formation of fully branched dendritic units)<sup>[56]</sup> or postsynthetic modifications.<sup>[57]</sup> It has to be stressed, that the DB is only an accurate topological parameter for hyperbranched polymers obtained in a random polymerization process. Since it is calculated from the fractions of building units as global parameters, the DB contains no information on the microstructure (e.g., in amylopectin) and topological isomerism.<sup>[56, 57]</sup>

### Conclusion

Although the foundations for hyperbranched polymers have been laid long ago by Flory, Gordon, and Burchard,<sup>[1, 4, 58]</sup> based on improved synthetic concepts such polymers with branch-on-branch topology have seen a vigorous renaissance only in recent years. The emergence of the perfectly branched dendrimers has prompted efforts in polymer science to improve the fundamental understanding of both synthetic multibranching strategies and suitable characterization techniques for hyperbranched polymers. Such materials conveniently prepared in one step are likely to represent a cheap alternative for dendrimers in the future for a large variety of applications. Multibranching polymerizations can be realized by two fundamentally different principles: i) by specific catalysts (e.g., chain cleavage/chain transfer in polysaccharide synthesis, migration/insertion in polyolefin synthesis), and ii) by polymerization of AB<sub>2</sub>-type monomers that may possess latent or bilatent structures. At present, the achievable branching density of hyperbranched polyolefins is considerably lower than that of hyperbranched polymers obtained from the polymerization of AB<sub>2</sub> type monomers. Also polysaccharides, with the exception of the highly branched dextran, are less branched than AB<sub>2</sub>-type hyperbranched polymers and in that respect resemble AB<sub>2</sub>/AB copolymers.

The quest for easily accessible new AB<sub>2</sub> type monomers and novel mechanisms that permit control of the branching reactions is in progress. The first recently reported example of controlled multibranching polymerizations by using a latent AB<sub>2</sub>-monomer<sup>[50]</sup> has already shown the versatility of the concept to construct complex molecular architectures, for example, by copolymerization with other linear (functional) co-monomers<sup>[55]</sup> and postsynthetic modifications.<sup>[57, 59]</sup>

Two major differences exist even in the case of an ideally controlled multibranching polymerization with chain growth kinetics in comparison to linear chain polymerizations. Since the number of end groups continuously increases with DP<sub>n</sub>, i) the polydispersity ( $M_w/M_n$ ) can not approach 1.0<sup>[48]</sup> and ii) the coupling probability of a B group of the initiator B<sub>f</sub> depends on DP<sub>n</sub> (e.g., only a fraction of a monofunctional initiator B<sub>1</sub> will be incorporated into the polymer).<sup>[60]</sup>

For hyperbranched polymers prepared in a controlled one-step procedure, molecular weights can be tailored by the monomer/initiator ratio; this is in pronounced contrast to the discrete generation-based synthesis of dendrimers. Furthermore, incorporation of co-monomers either in random or block fashion can easily be realized to introduce specific properties. Intriguing fundamental questions are faced in the future: i) is structural perfection a prerequisite for dendrimer-like behavior (e.g., in host-guest chemistry, low melt and solution viscosity); ii) to which extent is polydispersity tolerable for advanced applications? Based on the controlled syntheses, the elucidation of precise structure-property relationships with respect to molecular weight as well as degree of branching of hyperbranched polymers promises to become an exciting area of polymer research in the near future.

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