ABSTRACT: In the last 12 years the field of hyperbranched polymers has been well established with a large variety of synthetic approaches and fundamental studies on structure and properties of these unique materials. However, new developments involving hyperbranched materials appeared recently, for example, different synthetic strategies, new reaction mechanisms, formation of more complex architectures, a deeper understanding of the branched structure and their kinetic development, and intensive studies on the material properties and possible applications. This demonstrates the high versatility and the possibilities that are still involved in hyperbranched polymers and render it one of the most active fields in polymer science with a very promising future. © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 2505–2525, 2000

Keywords: hyperbranched polymers; dendritic polymers; synthesis; characterization; application

Professor Dr. Brigitte Voit obtained the diploma and Ph.D. degree in Chemistry at the University Bayreuth with Professor Dr. Oskar Nuyken on the subject of diazosulfonate-containing polymers for application as photo resins. Her first contact with hyperbranched polyesters was during the postdoctoral work with Dr. Richard Turner at Eastman Kodak in 1991. After this, she moved to the Technical University Munich where she obtained her habilitation degree on the topic of dendritic macromolecules in 1996. At present she is a full professor for Organic Chemistry of Polymers at the Technical University Dresden and she is heading the Subinstitute for Macromolecular Chemistry at the Institute of Polymer Research in Dresden. Her major interests are in polymers with special architectures, for example, hyperbranched polymers, block and graft copolymers, as well as in photo- and thermolabile polymers.
INTRODUCTION

Two years ago, Young Kim\textsuperscript{1} presented an excellent overview on “Hyperbranched Polymers 10 Years After” at the same location, which demonstrated very well that hyperbranched polymers can now be considered an established field in polymers science. Today, worldwide, the activities in this area are still extremely high as demonstrated by numerous reviews on hyperbranched polymers,\textsuperscript{2–7} dendritic molecules,\textsuperscript{8–17} or particularly on dendrimers\textsuperscript{18} are numerous. It became difficult to follow up all the activities and to keep track of the new structures appearing in the literature. Clearly, different aspects of synthesis, preparation of new structures, structure–property relationships, application prospects, and also theoretical aspects of kinetics and the degree of branching dominate. Recent developments in this field from my personal view will be the focus of the present review. But before starting with this, a brief journey back will be allowed.

When I was introduced into the field of hyperbranched polymers in 1991 it was symptomatic for the time that the initiative came not from academia but from industry. Richard Turner at Eastman Kodak was looking for a postdoc who was going to study the properties of hyperbranched polyesters. His interest was certainly influenced by recent publications in the field of dendrimers\textsuperscript{13,19–22} and a close cooperation with the group of Jean Fréchet. But, while perfectly branched dendrimers emerged from academia, from the beginning hyperbranched polymers were related to activities at industry\textsuperscript{23} as was also pointed out by Kim.\textsuperscript{1} The reasons for this are quite clear: it was obvious from the beginning that the step-by-step synthesis of dendrimers will restrict industrial application on a larger scale, whereas the random introduction of branching, for example, into polycondensates, was a well-established technique, which could be combined with known technical processes. In addition, the concept of highly branched, but irregular structures was well known for biopolymers, for example, polysaccharides,\textsuperscript{24} for low-density polyethylene,\textsuperscript{25} poly(ethyleneimine)\textsuperscript{26} and, of course, for polymer networks.\textsuperscript{27,28} But at this time, little was known on the properties of synthetic polymer structures with branching in each repeating unit (branch-on-branch topology) but without resulting in a crosslinked system. Everybody referred to the theoretical work of Flory\textsuperscript{28} who described the random AB\textsubscript{x} polycondensation theoretically already in 1952. Only few experimental data\textsuperscript{29–34} were already available, some of them even neglected or missed at this time since the term hyperbranched polymers was not used. Therefore, it was understandable that the main interest in the early 90th was to produce a reasonable amount of a hyperbranched polymer for being able to study the branched structure and especially the related material properties. The question arose whether hyperbranched polymers are something special compared to known branched polymers and further, is it possible to achieve new, interesting material properties, which can be clearly correlated to the highly branched and assumed globular structure. Today these questions still cannot be considered as fully answered, even though several application aspects of hyperbranched polymers, for example, in blends\textsuperscript{35–43} and coatings\textsuperscript{44–46} have been explored successfully by now.

In 1991, dendrimers entitled by different names (starburst dendrimers,\textsuperscript{13} arborols,\textsuperscript{21} cascade polymers\textsuperscript{22}) were already established and the differentiation towards the “dirty” imperfect hyperbranched structures prepared in a one-step synthesis was finalized. The name “hyperbranched polymers” for the latter as given by Kim and Webster\textsuperscript{52} indicated clearly that there is only a limited analogy to dendrimers and a close relation to the classical introduction of branching into a polymer chain. Today, however, both structures, dendrimers as well as hyperbranched polymers, are often discussed together using the term dendritic polymers. In many cases, the hyperbranched polymers are discussed as a more rapidly prepared and more economical replacement for perfect dendrimers in special applications. Today it is known that this is true for many aspects, for example, both types of branched structures exhibit a higher solubility and a lower solution viscosity compared to linear analogues.\textsuperscript{47,48} In addition, the large number of functional groups offers the possibility for further modification and special applications, and the type of end groups determines to a considerable extent the properties, for example, glass-transition temperature,\textsuperscript{49–52} of both classes of branched polymers. Nevertheless, there are also distinct differences between dendrimers and hyperbranched polymers. The most prominent feature of hyperbranched polymers is their “degree of branching,”\textsuperscript{54} $DB$ or the “branching factor,”\textsuperscript{33} which defines the ratio of branched, terminal, and linear units in the polymer structure. By definition $DB$ is 100\% for dendrimers and $<100\%$ (50\% for a statistical growth) for hyperbranched structures. Furthermore, hyperbranched polymers exhibit typical polymer features, as a broad molar mass distribution, isomerism, and an irregular growth with a statistical distribution of the functional groups throughout the structure. Often, they are even considered as having more resemblance with networks (just before the gel point)\textsuperscript{53–55} than with dendrimers. The high symmetry of the perfectly branched dendrimers, which allows a full mathematical description of the molecules, their repetitive synthesis, and the lack of a molar mass distribution assuming ideal growth, shifts dendrimers more towards
the area of large organic molecules or biomolecules than towards classical polymers.

The Classical Synthetic Approach

In the classical approach towards hyperbranched polymers, which goes back to Flory’s early description as a special type of polycondensation, $AB_x$ monomers with equal reactivity of the $B$ functionalities are condensed (Scheme 1). The reaction involves the typical features of a step growth reaction of multifunctional monomers and the formed oligomers but without the danger of crosslinking. Dendritic (fully reacted $B$ functions), terminal (no reacted $B$ function), and linear (one reacted $B$ function) units and one focal unit (A function) should be present in the resulting, highly branched macromolecule.

The use of $AB_3$ monomers predominates the synthetic approaches leading to a very broad structural variety in hyperbranched products. $AB_3$ and very few $AB_4$ and even $AB_6$ monomers are also reported in order to control the branching pattern. Even though a C—C coupling reaction was used for one of the first published $AB_2$-type polymers, polyester structures were favored clearly by many authors due to the availability of suitable monomers. Polyamides, polyurethanes, polyethers, poly(ethersulfone)s and -ketones, poly(phenylacetylene)s, and also polysiloxysilcarbodisiloxanes were also readily synthesized. For successful synthesis of classical hyperbranched polymers from $AB_2$ monomers, certain requirements have to be fulfilled, as the absence of side reactions, equal reactivity of the two $B$ functionalities, and no internal cyclization reactions limiting the achievable molar mass. It was found that the occurrence of cyclization reactions depends strongly on the monomer structure. Whereas the aliphatic monomer 2,2-dihydroxymethyl propionic acid leads to hyperbranched polymers with up to 92% cyclics instead of the focal $A$ unit, as verified by MALDI-TOF measurements, Hawker et al. could verify that up to 95% of the hyperbranched macromolecules prepared from 4,4′-dihydroxyphenyl-propionic acid still contain the acid focal unit.

Continuously, many new aspects are being found in the synthesis of hyperbranched polymers following the classical approach (Scheme 1), for example, improvement of the speed of the reaction by new reaction conditions and activation of monomers as described by Moore et al. for hyperbranched aromatic poly(etherimide)s. After only 2.5 min reaction time the hyperbranched product could be isolated using a rapid catalytic arylation method and the $t$-butyldimethylsilyl protected diphenol 1. The degree of branching in this product strongly deviated with 67% from the statistical value of 50% for equal reactivity of the $B$ groups in $AB_2$ monomers. DSM company developed a new hyperbranched poly(esteramide) (Hybrane™) with alcoholic end groups from $AB_2$ monomers (e.g., 2) based on different anhydrides and diisopropanolamine. The polycondensation proceeds when a slight excess of diisopropylamine is added without any catalyst at 140 °C. The material properties, especially the glass-transition temperature, is controlled by the used anhydrides and by end group modification. Hyper-
branched poly(ε-caprolactone) were achieved by esterification of AB2 macromonomers 3 and 4 (Scheme 2). Compound 3 resulted in hyperbranched structures with a degree of branching of only 37%, whereas the polymer based on 4 came close to a perfectly branched dendrimer. A novel AB2 monomers, p-(chloromethyl)phenylacetonitrile, in which the -CH2CN groups represents the B2 function and -CH2Cl the A group, was described by Jin et al. Using suitable reaction conditions, a soluble, hyperbranched polymer with cyano end groups was obtained. A very unusual hyperbranched polymer based on the reversible self-assembly of a organopalladium methylcyano complex has been reported by Rheinhoudt et al. Large organopalladium spheres with diameters of approximately 200 nm were obtained, which can be “degraded” to the monomer by addition of acetonitrile. These examples demonstrate that Flory’s presumption of an equal reactivity of the B functions might not be met in all synthetic examples.

Early on, the addition of a “core” molecule Bx (x ≥ 2) was explored (Scheme 1), mainly for better control over molar mass but also for control of the resulting geometrical shape. The most prominent example is the polycondensation of dihydroxymethylpropionic acid 6 in the presence of trimethylolpropane 5 (Scheme 3). In this case, a successive addition of the monomer also led to an increase in the degree of branching up to 67%. This effect was later described theoretically under the name “slow monomer addition” and verified by additional experiments by Frey et al.

Most recently, several groups recalled that the usually not commercially available AB2 can be substituted by conventional combination of A2 and B3 monomers (Scheme 1). Hyperbranched aromatic polyamides and polyethers (Scheme 4) have been obtained using combinations of monomers 7 + 8 and 9 + 5 when the reaction was stopped prior to the gel point. However, the critical conversion in these condensations is dependent on many factors, for example, the ratio of functionalities, purity of solvent and reagents, reaction time, and temperature. Therefore, it is very difficult to fully control the reaction and to obtain hyperbranched polymers with high molar mass without the need of separation of the sol from the resulting gel fraction. In addition, it could not be verified up to now that the growth and structure of the products are comparable to that of ABx polymers.

From the beginning, modification of the functional groups of hyperbranched polymers was of high interest in order to optimize material properties. This is primarily achieved by polymer analogous reactions on a preformed hyperbranched polymer, for example, as demonstrated in the alkyl modification of aliphatic and aromatic polyesters with a strong effect on the thermal and rheological properties of the resulting polymers. But also in situ end-group modification by direct addition of the modifying agent at the end of the polycondensation process and, as speciality, the internal functionalization of hyperbranched polymers by use of acetal-containing monomer units, which could later be deprotected leading to internal keto and hydroxyl groups, were reported.
Addition Reactions

Besides classical polycondensation reactions more and more addition reaction mechanism have been involved in the synthesis of hyperbranched polymers. This includes the above-mentioned reactions towards polyurethanes and polycarbosilanes involving the classical reactions of isocyanates and the hydrosilylation, but also more unusual addition reaction types. In Scheme 5, some monomers are listed, which have drawn my attention. The AB₂ monomer 10 can undergo a Diels–Alder [2+4] cycloaddition reaction leading to hyperbranched polyphenylenes,¹⁰⁶,¹⁰⁷ which can be planarized by a subsequent intramolecular cyclodehydration reaction. The building block 10—when the triple bond is blocked by triisopropylsilyl substituents—is also the basis for perfectly branched polyphenylene dendrimers.¹⁰⁶

Weber et al. used the ruthenium-catalyzed addition of ortho C—H bonds of acetophenone across a triple bond (11)¹⁰⁸ or a vinyl group (12),¹⁰⁹ the latter yielding only a DB of 12%. Scheme 6 pictures the proposed hyperbranched polymer structure from 11, which had a DB close to 60%.

We were able to prepare hyperbranched poly(ether- amide)s without encountering any side reactions via nucleophilic ring-opening addition reaction of phenols on oxazolines¹¹⁰ using the AB₂ monomer 13.¹¹¹ The thermally induced reaction proceeds in N-methylcaprolactame solution above 190 °C. The products are randomly branched with a degree of branching of 50% verified by high resolution NMR studies.

Hobson and Feast¹¹² used a Michael addition reaction of the AB₂ molecule 14, which leads to a hyperbranched polymer nearly identical to the PAMAM dendrimers of Tomalia.¹³ Surprisingly, the authors reported for the resulting hyperbranched poly(amideamine)s only terminal and dendritic units. No evidence for linear units could be found meaning a DB of 100% by the conventional definitions! Therefore, it was suggested that the formation of dendritic units is predominant due to special sterically or thermodynamically favored intermediates. This report started an intensive discussion on the degree of branching as a characteristic feature of hyperbranched polymers. Can DB be raised easily above the statistical value of 50%? Are hyperbranched polymers well described by DB? What are the topological differences between hyperbranched polymers with a DB of 100% and perfect dendrimers? Is it worthwhile to try to reach a DB of 100% from the material properties point of view?

We addressed this problem with the goal to intentionally prepare hyperbranched polymers that cannot contain any linear units. Again, an addition reaction was applied, the so-called [2+2] criss-cross cycloaddition of the bisazine 15 (Scheme 7).¹¹³ Because of the instability of the intermediate azomethinamine, which would represent the linear unit, the isolation of molecules with linear units is not possible in this case. The azomethinamine has to react back to a terminal unit or will add a second monomer to form a new dendritic unit. In the absence of any reagents, which can trap the unstable intermediate and therefore would lead to side products, a hyperbranched polymer with a degree of branching of 100% is formed. We could verify by intensive NMR studies that only the proposed dendritic and terminal units are present in the product.

However, as expected a broad molar mass distribution (PD = 2.2) was obtained via SEC analysis with $M_n$ in the range of 6000 g/mol. These materials can now be used to try to answer some of the above-posed questions.
Ring Opening

The example of the AB₂ monomer 13 demonstrated already, that ring-opening reactions have a substantial potential for the preparation of hyperbranched polymers. But, whereas still a classical random step growth reaction proceeds via 13 with equal reactivity of the functional groups B and following a known addition reaction mechanism, new monomers have been explored recently, which involve also new mechanisms, some of them closer to chain growth than step growth. These approaches have their origin in classical ring-opening reaction mechanism towards linear polymers, especially polyethers and polyesters. Chang and Fréchet¹¹⁴ reacted the bisepoxide 16 (Scheme 8) involving a proton transfer mechanism. In the first step of the polyreaction a proton is abstracted from the phenol group in 16 by an

---

Scheme 7. First steps of the criss-cross cycloaddition reaction of 15 with indication of the instable intermediate, which would represent a linear unit.¹¹³

Scheme 8. Monomers for ring-opening multibranching reactions.²⁶,¹¹⁴,¹¹⁶–¹¹⁸,¹²⁶,¹²⁷
OH to yield the phenolate. The nucleophile phenolate then adds to a second molecule 16 and opens one epoxide ring forming a dimer with a secondary alkoxide. This dimer does not propagate directly, first a proton exchange takes place with an unreacted monomer 16 yielding again the phenolate of 16, which reacts as nucleophile. An important feature in order to achieve this type of growth without undesired propagation through the nucleophilic center of the secondary alkoxide is that the phenolate formation in 16 is significantly faster than the nucleophilic propagation step. The much lower pKₐ (pKₐ ∼ 10) of the phenolic group relative to that of the secondary alkoxide obtained by epoxide ring opening (pKₐ ∼ 17) enables the fast proton exchange. Interestingly, the molar mass increases still exponentially with conversion as observed for the classical hyperbranched polycondensations.28,55,88,115 The authors stated that the polymerization mechanism is much more complicated than that of a classical polycondensation especially due to the increased possibility of intramolecular cyclization, a problem that was addressed generally for all hyperbranched polymers by Dušek et al.88

As mentioned before, commercial poly(ethyleneimine)26 prepared by self-condensing, ring-opening reaction of aziridine 17 is a branched polymer due to further reaction of the NH groups in the formed polymer chain with the cyclic monomer. Following the same principle, nearly at the same time Penczek et al.116 and Hult et al.117 published the successful cationic ring-opening polymerization of 3-ethyl-3-(hydroxymethyl)oxetane 18 leading to hyperbranched aliphatic polyethers with a degree of branching in the range of 41%117 and molar masses 18 around 2000 to 5000 g/mol. Some preliminary results on this reaction could also be obtained by Kim.1 Benzyltetramethylenesulfonium hexafluoroantimonate, BF₃O(C₂H₅)₂ or CF₃SO₃H have been applied as initiators and trimethylolpropane 5 was added as core molecule. The reaction proceeds via protonation of the oxygen in the oxetane ring, followed by ring opening due to nucleophilic attack of a second monomer (active chain end mechanism).116 However, in addition, two hydroxy-methylene functions can be condensed under acid catalysis forming an ether bond (activated monomer mechanism),116 which results in identical repeating units. The important reaction leading to branched units is a chain transfer process where the protonated oxetane ring can react with any hydroxyl group present in the system (pending in the linear repeating units or in a monomer). The DB value below 50% indicates that this chain transfer process proceeds with a lower probability than the growth reaction step.

Following the same line but using a different mechanism, Fréchet and coworkers118 published the formation of hyperbranched polyesters based on 5-(2-hydroxyethyl)-ε-caprolactone 19. The monomer looks first like an AB monomer and changes to a AB₂ type after the first addition of a second monomer (Scheme 9). The propagation and initiation proceeds entirely through one type of reactive nucleophil: a primary alcohol. Bulk polymerization of 19 in the presence of stannous octoate as catalyst yielded in hyperbranched polymers of M_w = 65,000–85,000 g/mol (M_w/M_n = 3.2) and a DB of 50% indicating equal reactivity of both primary alcohol groups.

It has also been known for some time that the polyreaction of glycidol 22 results in branched polymers119,120 (Scheme 10). Frey et al.121 described now the anionic ROMBP (= ring-opening multibranching polymerization) of 22, which they consider a latent AB₂. The polymerization proved to be very versatile and leads to hyperbranched polymers with rather narrow molar mass distribution (M_w/M_n = 1.1–1.4) due to a livinglike character of the reaction when only partial deprotonation to the initiating alkoxide (initiating site) of triol 5 was performed. This leads to a more or less simultaneous growth of all chain ends. After deprotonation of 5, the resulting alkoxide reacts

![Scheme 9. Ring-opening multibranching polymerization of glycidol.121](image-url)
with the unsubstituted end of 22 and thereby generates a secondary alkoxide. In contrast to the cationic polymerization of 22 described by Penczek and Dworak,120 a nucleophilic attack on the substituted end of the epoxide ring was observed. By use of the trifunctional initiator (core molecule) and slow monomer addition, cyclization was suppressed and the molar mass and polydispersity was controlled. The degree of branching was determined to be 53 to 59%, which is somewhat lower as expected for the slow monomer approach (67%).95 Molar masses $M_n$ between 2000 and 12,000 g/mol and polydispersity < 1.5 are reported. This approach opens now a pathway to very interesting, water soluble and biocompatible, aliphatic polyethers,122 which can be readily modified for use, for example, in star polymers,123 as nanocapsules124 for dye carriage, or as chiral and liquid crystalline material.125

In this respect, it should be mentioned that a very interesting approach towards hyperbranched polyamines using a multibranching polymerization type ring-opening reaction has been published by Suzuki et al.126 already in 1992, based on the cyclic carbamate 20 (Scheme 8). The approach was further extended towards 21 in 1998.127 In this case, the monomer has no resemblance to any ABB’ or AB2 monomer discussed up to now. Growth occurs only when an initiator with an active B group is added together with a catalyst. Scheme 11 gives the reaction pathway as proposed by the authors.126 Upon Pd-catalyzed activation of the allyl functionality, an amine attacks nucleophilicly the allylic position, the cyclic structures is opened under evolution of carbon dioxide; this liberates a free amino function, which is now equivalent to a B$_2$ group. Secondary and primary amines can react with the allyl group leading to linear or dendritic structural units. Further modification of the primary and secondary amino functions with n-BuNCO facilitated storage and characterization of the resulting products from 21 and 22.127 Thus, molar mass determination became possible resulting in $M_n$ values between 1800 and 5300 g/mol (GPC or VPO) and rather narrow molar mass distributions ($M_w/M_n = 1.3–1.5$). DB was calculated from NMR data to be 60–80%. The authors state that the positive deviation of the DB is a result of the higher nucleophilicity of the secondary amine in polar solvents compared to the primary ones.

These examples demonstrate the trend in the synthesis of hyperbranched polymers towards the exploration of new reactions types and integration of chain growth mechanism. Reasons for this are the strive for better control of structure and polydispersity in hyperbranched polymers. Monomers as those described by Suzuki et al. allow even to fully suppress the self-condensation of the monomers and strictly force a growth at the chain end.

Self-Condensing Vinyl Polymerization

The trend towards chain growth mechanism is well demonstrated by the growing importance of the self-condens-
ing vinyl polymerization (SCVP), described the first time by Frechet et al.\textsuperscript{128} in 1995 for the synthesis of hyperbranched polymers (Scheme 12). SCVP is based on a vinyl monomer that additionally bears an initiating group (\textit{“inimer”} = initiator + monomer). These monomers allow propagation through the double bond (= chain growth) and condensation of the initiating site with the double bond (= step growth). This potential has been observed already by Nuyken et al.\textsuperscript{129} in the living cationic copolymerization of 4-(chloromethyl)styrene \textsuperscript{23} (Scheme 13) and isobutylene since a significant amount of branch points had been found in the attempted linear macroinitiator. The living cationic polymerization of 3-(1-chloroethyl)ethenylbenzene \textsuperscript{24} at low temperature using SnCl\textsubscript{4} was also the basis for the first successful synthesis of hyperbranched polymers.\textsuperscript{128} Polymers with low Mark–Houwink constants were achieved as typical for globular structures. More recently, 1-[(2-vinylxy)-ethoxy]ethyl acetate\textsuperscript{130} \textsuperscript{25} was polymerized cationically using ZnCl\textsubscript{2} as activator leading to hyperbranched polymers of $M_n < 5000$ g/mol and very broad polydispersities of 7–10; no information on DB is given in this case.

This process has been readily extended towards other controlled chain growth mechanism, especially group transfer polymerization\textsuperscript{131,132} using 26, and controlled radical polymerization both via TEMPO\textsuperscript{133} (27) and via atom transfer radical polymerization (ATRP)\textsuperscript{134–136} (23, 28, 29). Scheme 13 depicts a selection of used SCVP monomers. A general feature of SCVP is the unequal reactivity between chain growth of the vinyl group and step growth through the initiating site. Therefore, also the degree of branching can differ strongly from the value 50\% of the random AB\textsubscript{2} condensation. Frechet\textsuperscript{134} demonstrated that just by varying the reaction conditions the DB achieved in the metal catalyzed “living” radical polymerization of 4-chloromethylstyrene \textsuperscript{23} can be varied from nearly zero (linear polymer) to highly branched. Matyjaszewski et al.\textsuperscript{135} used preferentially the acrylate monomer 28 compared to 29 in ATRP since 29 might lead to a lower DB. The danger of side reactions (elimination, radical coupling) limits also the use of controlled radical processes. Especially at longer reaction times a gel fraction can no longer be avoided. Nuyken and Wieland\textsuperscript{137} recently developed a concept to use the azo group containing vinyl monomers 30 for the preparation of highly branched polymers also via a radical process. It is proposed that the methyl malonodinitrile radical, which is set free after azo decomposition, acts as reversible terminating agent but not as initiator, therefore no indica-

\begin{center}
\textbf{Scheme 11.} Proposed reaction scheme for 20 by Suzuki and coworkers.\textsuperscript{126}
\end{center}

\begin{center}
\textbf{Scheme 12.} Scheme of the self condensing vinyl polymerization SCVP (adapted from Fréchet et al.\textsuperscript{128}).
\end{center}
tion of crosslinking was observed even in the homopo-
lymerization of 30. Light scattering and viscosity mea-
surements indicated a globular structure of the products.

Often in SCVP it is not possible to determine the DB
directly via NMR analysis. Therefore, indirect methods,
for example, viscosity measurements and light scattering
methods selective towards the more globular structure of
a hyperbranched polymer, have to be used. The polydis-
persities are usually very high and represent the presum-
ably nonliving character of the reaction. However, the
big advantage is the extension of the concept of hyper-
branched polymers towards vinyl monomers and chain
growth processes, which opens unexpected possibilities.
In addition, the mechanism and kinetics of SCVP,
molar mass, and polydispersity development with con-
version, the degree of branching, influence of a
core molecule as well as effect of different reaction
rate constants has been treated theoretically quite ex-
tensively. These efforts are representative for the in-
creased interest in theoretical aspects of hyperbranched
polymers.

Theoretical Treatments
First theoretical considerations especially on statistics,
on molar mass evolution, and polydispersity of hyper-
branched polymers based on ABx monomers were pub-
lished by Flory. These studies were deepened by Bur-
chard in the 70s. But with the increasing interest in
synthetic aspects of hyperbranched polymers also the
theoretical aspects had been reconsidered. As mentioned
above, this was of special interest for the SCVP since in this case two different growth mechanisms are
involved and the monomers are of ABB’ type. Never-
theless, the obtained conclusions can be transferred
readily also towards classical ABx polyreactions as com-
parison of results obtained for SCVP with those derived
for ABx systems prove. Dušek could show how the
molar mass and the polydispersity can be limited by
internal cyclization reactions. Intensively, the degree of
branching and the influence of different reaction param-
eters, core molecules, copolymerization, and post modi-
fication steps were studied by Frey et al. Thus,
under special conditions, for example, slow monomer
addition, it was found that the degree of branching can be
increased from 50 to 67% even for a statistical process.
Post modification of polymers with branched units even
allows to “disguise” a linear polymer as a branched
one. This demonstrates that the value DB following
the accepted definitions is not fully suitable
for the description of the microstructural features and the
topology of hyperbranched polymers.

We were able to verify the proposed development of
the branched units with conversion by experimental stud-
ies on the polycondensation of 4,4-bis-(4‘-hydroxyphen-
yl)pentanoic acid, a monomer that was known for a low
tendency of internal cyclization and a high probability
for an undisturbed statistical growth with equal reactivity
of the B functions (DB = 50%). The development of
different structural units with conversion and even the
development of structural diads could be followed by use
of high resolution NMR analysis. However, this ideal
case of equal reactivity of the B functions cannot be
assumed for all real hyperbranched reactions, particularly
if SCVP or new addition and ring-opening reactions
(latent AB2 monomers) are applied as shown above.
Therefore, unequal rate constants have to be considered and incorporated into theoretical treatments. This was already discussed by Frey and Müller. A detailed theoretical treatment, which can be applied to any reaction with unequal reaction constants was developed also recently in our own group. An experimental application of this theoretical derivation has been done on the example of the polycondensation of 3,5-bis(trimethylsilyloxy)benzoyl chloride, which usually leads to a DB of 60 to 65%.

Hyperbranched Polyethylene

Branching is a very well known aspect in polyethylene chemistry, either as uncontrolled long chain branching in low density polyethylene LDPE (high pressure, radical process) or as intended short chain branching in linear low density polyethylene LLDPE (copolymerization). Recently, Brookhart et al. and then Guan et al. reported the formation of highly branched (“hyperbranched”) polyethylene at low pressure by a so-called “chain walking” process using palladium(II) and nickel(II) catalysts, which contained very bulky chelating diimine ligands. Even higher branching was observed by Sen et al. with a [Ni(π-methallyl)(Br)] or a Pd(1,5-cyclooctadiene)(Me)(Cl) catalyst. “Chain walking” or better isomerization of the active site to the internal backbone during polymerization was reported already by Fink and coworkers in 1985 for α-olefins. Now, it could be shown that the polyethylene topology can be well controlled from nearly linear to hyperbranched just by the reaction pressure. Scheme 14 summarizes the schematic mechanism as proposed by Guan. The change in topology could be verified by differences in hydrodynamic radius and solution viscosity for samples prepared at different pressure but with similar $M_w$ as determined by MALS.

The example of these highly branched polyolefins demonstrates the trend to broaden the expression hyperbranched or dendritic to much more complex architectures no longer solely based on AB or related monomers.

Arborescent Graft and Comburst Polymers

The concept of very highly, irregularly branched polymer topologies is realized intriguingly in the so-called “comburst” (by Tomalia) and arborescent graft polymers (by Gauthier). Here, first linear polymer chains with functional sites are prepared. By subsequent “branch on grafting” preferably with polymer chains of defined molar mass, very rapidly products with extremely high molar mass are obtained. Both types of grafting are possible; “grafting onto” based on preformed living polymer chains and “grafting from” using polymeric bound initiating sites (Scheme 15 (a)).

By living anionic “grafting onto” polystyrene, polybutadiene, (and polyethylenes after hydrogenation), poly(ethyleneoxide) and also polystyrene-co-polyisoprene arborescent graft polymers could be achieved. Core-shell molecules with amphiphilic properties are reported by polystyrene-co-poly(ethyleneoxide).
arborescent polymers. These polymers with molar masses $M_w$ up to $7 \times 10^7$ and $M_w/M_n < 1.3$ are completely soluble and exhibit comparable low solution viscosities. In melt rheology studies these macromolecules showed a viscous flow behavior and resembled gels just before the gel point. The most highly branched arborescent graft polymers display a frequency dependence similar to crosslinked networks or microgels. The overall shape of the molecules can be influenced by changing the arm length or the grafting density. The former can be readily controlled by varying the ratio monomer to initiator. Light scattering measurements showed that the polymers behave in solution as hard spheres. Sheiko et al. could visualize arborescent graft polystyrenes with different branching density as monolayer films cast on mica. The polymers were depicted as distinct hexagonally packed globuli (Scheme 16) whose size was consistent with molecular dimensions obtained from viscosity and dynamic light scattering measurements. The layer thickness and the particle dimensions depend on the branching density. Molecules with a high branching density (on average 500 g/mol between branch points) recovered a spherical geometry after annealing above the glass-transition temperature. In the case of lower branching density (on average 2000 g/mol between branch points) a pancake structure remained stable after annealing. This demonstrates that arborescent graft polymers represent a peculiar type of colloidal particles possessing a topological defined surface.

The combination of a dendritic unit with a linear polymer chain has been extensively studied for perfectly branched dendrons leading to complex architectures, for example, dendron-linear block copolymers, dendronized or monodendron jacketed linear polymers, and to star polymers with a dendritic core. Especially the attachment of monodendrons to a linear polymer chain by postmodification or by polymerization of monodendron-containing macromonomers draw much attention due to the visualization of these stiffened polymer chains as single molecules by AFM (Scheme 17).

The preparation of more complex architectures using hyperbranched macromolecules, however, is a much more recent trend. Here, especially the field of star polymers with a hyperbranched core has been explored. Free radical, controlled radical, ring-opening, anionic, and cationic polymerizations have
been applied using hyperbranched macrorinitiators. The resulting polymers show typical behavior of star polymers, for example, low solution viscosities nearly independent from molar mass. By combination of suitable core/arm combinations, structures with amphiphilic properties can be obtained. Scheme 18 depicts the synthesis of star polymers with a relatively unpolar hyperbranched polyester core and polar poly(methyloxazoline) arms.188 Wang et al.191 produced electrically conducting star polymers with a hyperbranched polyphenylene core and polythiophene arms.

A triblock copolymer A-B-A with A consisting of hyperbranched polyesters from 3,5-dihydroxybenzoic acid and B being an oligo(etherketone) was reported by Kricheldorf et al.192 The triblock was prepared by copolycondensation of the telechelic oligomer with AB₂ monomers. The polymer proved to be fully soluble in THF due to the hyperbranched structural components.

Hyperbranched Polymers and Surfaces

The modification of surfaces and thin polymer films dominates recent activities in polymer science. Therefore, it is not surprising that dendrimers—and in some cases also hyperbranched polymers—have been studied on surfaces. This covers the field of the visualization of single dendritic macromolecules in order to get information on their shape and size (see sections above and, e.g., refs.193–196), but also the use of dendrimers as carriers for metal ions,197 change of surface adhesion by grafting with dendrons198 or studies on thin films (monolayers, self-assemblies) of dendrimers with electrical, catalytic, or sensoric properties.199

The properties of hyperbranched polymers on surfaces have been studied up to now only seldom, but it can be expected that this aspect will develop rapidly. One example is the study of surface morphology and friction of thin films from hyperbranched perfluorinated polymers in dependence of the length of perfluoroalkyl chains by AFM.200 Quite intensively, arborescent surface grafted poly(acrylic acid) has been explored by Crooks and Bergbreiter201 for different applications (Scheme 19). Their interest covers surface patterning, biocompatibility, ion binding ability, and sensoric properties.

Following this line, we prepared recently thin polymer layers of aromatic hyperbranched polyesters with

![Scheme 16.](image-url)
different end groups on silica substrate and studied wetting and swelling behavior.²⁰²

Various Applications

Hyperbranched polymers were considered early on as suitable for any application where the low viscosity and the large number of functional groups are of advantage. Studies on material properties proved that the highly branched structure does not favor the formation of entanglements. Therefore, hyperbranched polymers are brittle and the determination of mechanical properties is mostly not possible due to difficulties in sample preparation. This limits certainly their application as bulk material, for example, as engineering plastics.

Application fields discussed for perfectly branched dendrimers, for example, in medicine as drug carrier molecules or in gene delivery, as standards or models for biomolecules or as catalytic active molecules, were also not considered seriously for hyperbranched polymers, since the lack of a well-defined structure and molar mass is a disadvantage in these sensitive areas.

But, as pointed out earlier, hyperbranched polymers draw much attention as blend components, additives, and primarily, as coating components. In the later, the high functionality (after modification, for example, with crosslinkable groups) in combination with the high solubility and low viscosity are excellent prerequisites for use in high solid coatings or powder coatings. Hyperbranched polymers with acrylate, vinyl ether, allyl ether,

Scheme 17. (a) Suggested conformation of monodendron jacketed linear chains; (b) SFM-micrograph of single monodendron jacketed (polyether, G1) polystyrene molecules with \( \langle M_{n\text{monomer}} \rangle = 1194 \, \text{g/mol}; \langle M_{n\text{polymer}} \rangle = 1.1 \times 10^6 \, \text{g/mol}, M_n/M_w = 2.6 \) on highly oriented pyrolitic graphite.¹⁷⁶ (The pictures have been supplied very kindly by S. Sheiko and M. Möller).

Scheme 18. Amphiphilic star polymers via “grafting from” with a hyperbranched polyester core and polar poly(methyloxazoline) arms.¹⁸⁸
epoxy, and OH-functions were studied as multifunctional crosslinker in coatings and in thermosets. Recently, also the application of OH terminated hyperbranched polyesters in low volatile organic compounds (VOC) polyurethane coatings has been explored. As a general feature of hyperbranched polymers in crosslinking reactions we concluded that a very high functionality number can lead to a too fast crosslinking reaction and therefore solidification of the material before all reactive functions had the chance to react. Therefore, the number of reactive groups has to be balanced and reactive diluents should be used in coatings with hyperbranched components.

The application of hyperbranched polymers (and also arborescent graft polymers) in processing as melt modifier, additive, or as blend component is also widespread. Kim et al. showed that blends of hyperbranched polyphenylene and linear polystyrene exhibit a reduced viscosity at high temperatures and shear rates and an improved thermal stability compared to pure polystyrene. When hyperbranched polyesters were blended with linear polyesters, polyamides, and polycarbonate as described by Massa and coworkers, mostly full miscibility was observed due to strong hydrogen bonding. The partially miscible polycarbonate blends exhibited an increase in the tensile and compression modulus but loss in toughness. Modified hyperbranched polyesters were used as dye carrier in polyolefine blends. The resulting materials showed a reduced melt viscosity and a homogeneous distribution of the dye in the matrix. The fact that alkyl modified hyperbranched polyesters or polyethers show amphiphilic character and can act as carrier molecules for physically enclosed organic molecules (for example, organic dyes) like in nanocapsules or in the dendritic box opens many new application fields not only as additive carrier for thermoplastics (Scheme 20).

Scheme 19. Surface arborescent graft polyacrylic acid on a self-assembly monolayer confined to a gold substrate as depicted by Crooks and coworkers [MUA = mercapto undecanoic acid; PAAM-c-PAA = random copolymer of poly(acrylic acid) and poly(acrylamide) formed from PAA carboxylic acid groups and the amines of hydrolyzed amine terminated poly(t-butyl acrylate)].

Scheme 20. Schematic representation of the diffusion of organic dyes into an amphiphilic hyperbranched polyester (aromatic hb polyester modified with C12-alkyl side chains, D = organic dye) and the subsequent incorporation into a polyolefin matrix.
Hong et al.\textsuperscript{39} found a strong effect of alkyl modified aliphatic hyperbranched polyesters on the rheological behavior of polyethylene (LLDPE). Mulkern et al.\textsuperscript{210} reported a lubricant effect of hyperbranched polymers also in polystyrene blends. Recently Wahlen et al.\textsuperscript{211} observed the reinforcement of PA6 when hyperbranched fully aromatic polyamides were added during the polycondensation.

We studied blends of hyperbranched aromatic-aliphatic poly(etheramide)\textsuperscript{111} with commercial linear polyamide PA6.\textsuperscript{38} All blends showed full miscibility. Furthermore, the hyperbranched polymer had no significant negative influence on the melting and crystallization behavior of the PA6 matrix, the shear storage modulus was even increased. But the rheological investigations exhibited an unexpected strong reduction in melt viscosity even when only 0.1 wt % of hyperbranched polymer was added. With regard to the processing of PA6 the reduced melt viscosity without loss of mechanical properties implies interesting application aspects of hyperbranched polymers as processing aids.

Besides those more classical application aspects in commodity and engineering plastics, also new areas are explored for the use of hyperbranched polymers. One covers the formation of nanofoams. Globular, hyperbranched molecules, which are degradable can act as pore forming material for a nanoporous system. For this, however, dispersion of the hyperbranched polymer on a molecular level in a stable matrix is required. The nanopoous material is for example, of interest in chromatography and for the formation of aerogels and xerogels. Hence, Bourn et al.\textsuperscript{212} described the use of dendrimers and arboroles with carbosilane cores for the preparation of hybrid xerogels. In this regard, Muzafarov et al.\textsuperscript{213} studied the degradation behavior of hyperbranched poly[bis(undecenyloxy)methylsilane]. Of high interest is also the preparation of nanoporous polymers as low dielectric constant material for use as novel interlayer dielectric material (ILD).\textsuperscript{214} Already realized porous systems have reached dielectric constants from $\varepsilon_r = 2.5$ to approximately 1 as found for aerogels.\textsuperscript{216} The decrease of $\varepsilon_r$ is given by the inclusion of air filled cavities, which might be formed by degradable star or dendritic polymers (Dendriglas \textsuperscript{30}\textsuperscript{217}) or by phase separated block copolymers with labile segments.\textsuperscript{218–220} Hyperbranched poly(aryl ether phenylquinoxaline)\textsuperscript{221} were used for structure control in organic–inorganic hybrids for application in microelectronics. We selected as labile moiety for degradable hyperbranched polymers, the triazene group,\textsuperscript{222} which is known to be photolabile and can be degraded into volatiles for example, upon laser ablation.\textsuperscript{223} As depicted in Scheme 21, the AB\textsubscript{2} monomer \textit{31} containing the labile unit was condensed under mild polycondensation conditions to a degradable polyester.\textsuperscript{224}

Recently, also the use of hyperbranched polymers were reported in sensorics,\textsuperscript{201,202} as nonlinear optic\textsuperscript{225} and LC material,\textsuperscript{125,226,227} for ion conductivity,\textsuperscript{228} in molecular imprinting,\textsuperscript{229} in catalysis,\textsuperscript{230} and also as soluble functional supports.\textsuperscript{122,231} These examples demonstrate the very broad perspectives of hyperbranched polymers in all areas of modern polymer science.

Where to Go?

Only very few areas in the field of polymer science have drawn that much interest in the last decade as dendritic macromolecules. These branched structures have a large input not only on organic, polymer, and physical chemists but also to a large extent on physicists, biologists and biochemists, biomedical groups, and theoreticians. They opened a new view towards the possibilities of branching and topology in polymers with regard to synthetic challenges but also for new application areas.

But, one can clearly see that we just left the starting line in the field of hyperbranched polymers. In the last few years the goal to prepare new and more complex hyperbranched structures to be able to explore the full potential of this polymer class, led to significant new
REFERENCES AND NOTES

40. Carr, P. L.; Davies, G. R.; Feast, W. J.; Stainton, N. M. Polymer 1996, 37, 2395.


