Hyperbranched and Highly Branched Polymer Architectures—Synthetic Strategies and Major Characterization Aspects

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1. Introduction

"Life is branched" was the motto of a special issue of *Macromolecular Chemistry and Physics*[1] on "Branched Polymers", indicating that branching is of similar importance in the world of synthetic macromolecules as it is in nature. The significance of branched macromolecules has evolved over the last 30 years from just being considered as a side reaction in polymerization or as a precursor step in the formation of networks. Important to this change in perception of branching was the concept of "polymer architectures", which formed on new star- and graft-branched structures in the 1980s and then in the early 1990s on dendrimers and dendritic polymers. Today, clearly, controlled branching is considered to be a major aspect in the design of macromolecules and functional material.

Hyperbranched (hb) polymers are a special type of dendritic polymers and have as a common feature a very high branching density with the potential of branching in each repeating unit. They are usually prepared in a one-pot synthesis, which limits the control on molar mass and branching accuracy and leads to "heterogeneous" products with a distribution in molar mass and branching. This distinguishes hyperbranched polymers from perfectly branched and monodisperse dendrimers. In the last 20 years, both classes of dendritic polymers, dendrimers as well as hb polymers, have attracted major attention because of their interesting properties resulting from the branched architecture as well as the high number of functional groups.[2] The challenging synthesis of the dendrimers attracted especially scientists with a strong organic chemistry background and led to beautifully designed macromolecules, which allowed a deeper insight into the effect of branching and functionality. Dendrimers have been considered as perfect "nano-objects" where one can control perfectly size and functionality, which is of high interest in nanotechnology and biomedicine.

hb polymers, however, were considered from the beginning as products suitable for larger-scale application in typical polymer fields like coatings and resins, where a perfect structure is sacrificed for an easy and affordable synthetic route. Thus, the first structures that were reported paralleled the chemistry used for linear polymers like typical polycondensation for polyester synthesis. More recently, unconventional synthetic methods have been adopted also for hb polymers and related structures. Presently, a vast variety of highly branched structures have been realized and studied regarding their properties and potential application fields. Excellent reviews appeared covering synthesis strategies, properties, and applications, like the very recent tutorial by Carlmark et al.,[3] the comprehensive book on hyperbranched polymers covering extensively synthesis and application

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Albena Lederer obtained her Ph.D. in 1999 from the University of Mainz after her research in the field of physical chemistry of polymers at Max-Planck-Institute of Polymer Research Mainz. Since 2000 she is extensively investigating the physicochemical properties of branched macromolecules. Since 2007 Albena Lederer is leader of the Polymer Separation group at the Leibniz-Institute of Polymer Research Dresden. To her main research area belong the characterization of dendritic and multifunctional polymers in solution and the development of new separation methods for branched polymers.

aspects[4] that is about to be published, and the reviews by Yan[5] and Hayes.[6]

Hyperbranched polymers have received much industrial attention and have been commercialized for several applications or are presently in the advanced development stage. One major use of commercial interest is as a reactive component in coating and resin formulations. Other potential applications include using these highly branched and highly functional polymers as polymer additives in linear polymers for improving rheology and flow and for surface modification. In addition, the excellent thermal stability that can be designed into a hb polymer as well as modulus properties qualify these products as interesting polymer additives. The commercial success of hb polymers is a result of the highly branched and dense but irregular structure that leads to

excellent solubility, compared to linear polymers, low solution viscosity, modified melt rheology, and high level of terminal end group functionality.[7−10]

In addition to "traditional" applications of hb polymers, the unique dendritic structure opens up opportunities for new "nanotechnology" applications based on specific confinement of functional units and the formation of pores and cavities, e.g., as in thin films in sensor devices and diagnostics, as porogens for nanofoams, and as carriers for special additives, catalytic species, and therapeutics.[5,6,11−14]
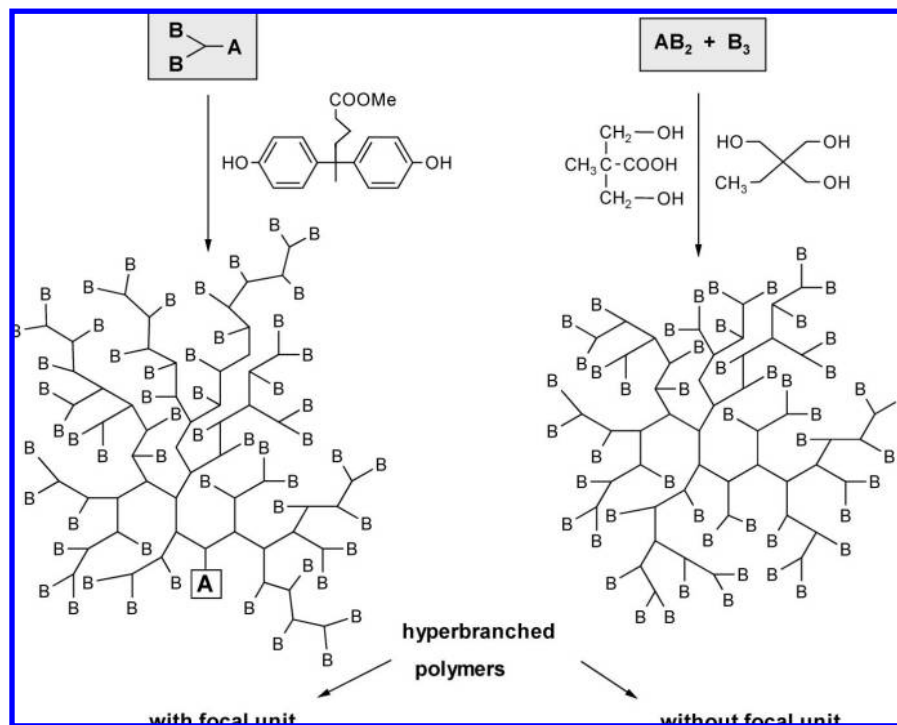
Polyesters dominate the field, with the Perstorp "Boltorn" products[10] leading in product development and with hyperbranched polyesters based on the relatively easily available bis(4-hydroxyphenyl) pentanoic acid (BHPPA) often used in academic studies.[15,16] However, the poly(esteramide)s commercialized by DSM under the trade name Hybrane,[9] poly(ethyleneimine)s from BASF SE under the trade name Lupasol,[17−19] and polyurethanes[17−19] and polyesters[20] developed as well at BASF SE are further examples for hyperbranched polymers specially suited for commercial coatings and resin application.[21] Hyperbranched polyglycerols, however, prepared by HyperPolymers[22] and more recently as self-assembled nanocapsules by Nanotransport Systems[23] have potential in biomedical applications, similar to the specially functionalized dendritic and hyperbranched polyesters based on bis(methylol)propionic acid as provided by Polymer Factory.[24]

This review will focus on the synthetic approaches used to prepare *hyperbranched* and *highly branched* polymers covering the classical lines but also giving special attention to the new trends to dilute the branching with linear polymer chains by creating increasingly complex linear-branched hybrid structures. Hyperbranched structures created on planar surfaces or on various (nano)particles and nanoscale objects and perfectly branched classical dendrimers and dendrons will be excluded from this review, since both topics are extensive and contain sufficient material for several individual reviews. Theoretical as well as application aspects will only be addressed peripherally to give background and perspectives for some of the presented synthetic aspects. The irregular branched structure in hb polymers and highly branched derivatives leads also to significant and new challenges in the characterization of these materials. Therefore, the last part of this review will be devoted to the structural characterization of hb polymers focusing on newly adapted and developed methods that help to define the special features of these highly branched and functional materials.

2. Synthesis of Hyperbranched Polymers

As already outlined, a vast variety of highly branched polymer structures has been reported since their theoretical treatment in the middle of the 20th century.[25] Especially in the last 20 years,[26,27] very strong synthetic activity emerged on macromolecules that can be classified as "hyperbranched" (hb).[27] This term now not only covers the "classical" products based on Flory's AB_x approach[25] but is extended to various highly branched structures including those prepared by the $A_2 + B_y$ monomer combination;[5,8,25,28,29] those prepared by self-condensing vinyl polymerization (SCVP),[30] ring-opening multibranching polymerization (ROMBP) or self-condensing ring-opening polymerization (SCROP), or proton transfer polymerization;[31−34] and those prepared by various copolymerizations and methodology combinations including self-assembly aspects, which lead to linear−highly branched

Scheme 1. Schematic Representation of the Synthesis of hb Polymers through the AB_x and $AB_x + B_y$ Approach ($x \geq 2$; Here, 2; $y \geq 3$; Here, 3)

hybrids like dendronized polymers,[35–37] dendrigrafts,[38–40] and hb core star-branched structures[41,42] and nanocapsules.[38,43]

Previous comprehensive reviews like that of Gao and Yan[5] provide an excellent overview of the different synthetic approaches to hb polymers. Gao and Yan pointed out that the first hyperbranched structures, based on an $A_2 + B_3$ approach, go back as early as Berzelius,[44] followed by an early paper on hb polyethers through AB_3 monomers by Hunter and Woolett.[45] Considering the $A_2 + B_y$, many resins actually fit the term "hyperbranched" in the form of a soluble precursor polymer ready for curing. Thus, an early example for hyperbranched structures was introduced by Korshak, who described the synthesis of branched polyphenylenes through cyclotrimerization of various diethynylbenzenes with phenylacetylenes.[46] These acetylene-terminated phenylene oligomers called H-resins were commercialized by Hercules, Inc., in 1974 (see review by P. M. Hergenrother[47]).

Further reviews on various synthetic aspects of hyperbranched polymers are given by Hayes,[6] Yan, Gao, and Frey,[4,5,48] Jikei,[8,49] Fréchet,[50] Hult,[10] Inoue,[11] Kim,[51] Kubisa,[34] Guan,[52] and Long,[53] as well as in our own work.[2,7,13,14]
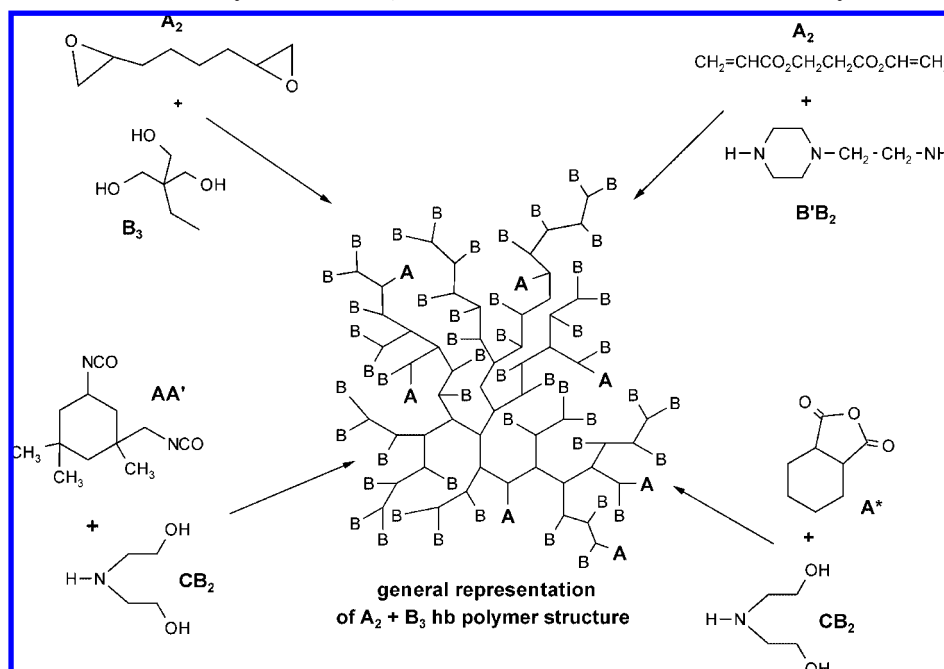
2.1. General Aspects and Methodologies

2.1.1. Step-Growth Approaches

AB_x and $AB_x + B_y$. In the classical approach toward hyperbranched polymers, which goes back to Flory's[25] early description as a special type of polycondensation, AB_x monomers with equal reactivity of the B functionalities are reacted (Scheme 1). The reaction involves the typical features of a step-growth reaction of multifunctional monomers and the formed oligomers but without the possibility of cross-linking. 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_2 monomers dominates the synthetic approaches, leading to a very broad structural variety in hyperbranched products. AB_3,[45,54–56] AB_4,[57,58] and even AB_6[58] monomers are also reported in order to control the branching pattern, but to a much lower extent. Even though a C–C coupling reaction[59] was used for one of the first published AB_2 polymers, polyester structures clearly were favored by many authors[15,26,60–66] due to the availability of suitable monomers. For successful synthesis of classical hyperbranched polymers from AB_x monomers, the following requirements have to be fulfilled: A must react selectively with B with the absence of side reactions, the B functionalities must have equal reactivity, and there should be no internal cyclization reactions that limit the achievable molar mass. It was found that the occurrence of cyclization reactions depends strongly on the monomer structure,[15,58,67] and their presence was first reported by Percec et al.[68] for liquid crystalline polyethers. Whereas the aliphatic monomer bis(methylol)propionic acid leads to hyperbranched polymers with up to 92% cyclics instead of the focal A unit as verified by MALDI-TOF measurements,[67] Hawker et al.[15] could verify that up to 95% of the hyperbranched macromolecules prepared from 4,4'-dihydroxyphenyl propionic acid still contain the acid focal unit. Besides cyclization reactions, also other side-reactions can occur, e.g., ether formation during polyester synthesis,[69] which can lead to cross-linking since in this case B functions react with other B functions. Moore et al. described the synthesis of hyperbranched aromatic polyetherimides from a trimethylsilyl protected diphenol as AB_2 monomer using a rapid catalytic arylation method.[70] The degree of branching (DB) in this product was 67%, which strongly deviated from the statistical value of 50% for equal reactivity of the B groups in AB_2 monomers. Similarly, the activated AB_2 monomer 3,5-bis(trimethoxysilane)benzoic acid chloride led in the bulk polycondensation to a degree of branching of >60% due to activation of the second branching

Scheme 2. Schematic Representation of the Synthesis of hb Polymers by Various $A_2 + B_y$ ($y \geq 3$) Approaches with Examples of Monomer Combinations (A^* Indicates Cyclic Monomer; AA' Indicates Differences in the Reactivity)

step.[71] These examples demonstrate that Flory's presumption of an equal reactivity of the B functions and absence of side-reactions might not be met in all synthetic examples.

Early on, the addition of a "core" molecule B_x ($x \geq 2$) was explored (Scheme 1), mainly for better control over molar mass but also for control of the resulting geometrical shape.[10,57,72] When a core molecule is used, the resulting products should no longer exhibit the focal unit A. This limits the molar mass buildup, and thus, the molar mass is controlled by the ratio B_x to AB_x. The most prominent example is the polycondensation of bis(methylol)propionic acid in the presence of trimethylolpropane.[57] In this case, control over the reaction was achieved by successive addition of monomer portions. This process is used for the industrial synthesis of Boltorn. This effect was later described theoretically under the term "slow monomer addition" and was verified by additional experiments by Frey et al., validating the fact that, theoretically, an increase in the degree of branching 67% can be expected under those conditions[73,74] However, it has to be pointed out that the portionwise addition of monomer corresponding to the amount necessary for stepwise dendrimer formation as used for the preparation of Boltron is not equivalent to the kinetics in a reaction with continuous slow feed of the monomer into the reaction vessel.

Even though bis(methylol)propionic acid seems to be the most easily available AB_2 monomer structure, in general, the resulting aliphatic Boltorn type hb polyesters still have some drawbacks regarding side-reactions during melt polycondensation (cyclics and ether formation, decarboxylation), which limit the achievable molar masses.[67,69]

However, complete incorporation of the core molecule into each hb macromolecule and in all molar mass fractions is not trivial and cannot always be achieved. Twyman et al.[75] showed that using an activated core moiety in a reversible polycondensation is an effective strategy for highly efficient core functionalization.

A general method to introduce functional end groups directly during the polyreaction is the addition of a monofunctional compound to an AB_x monomer ($AB_x + A$). Thus,
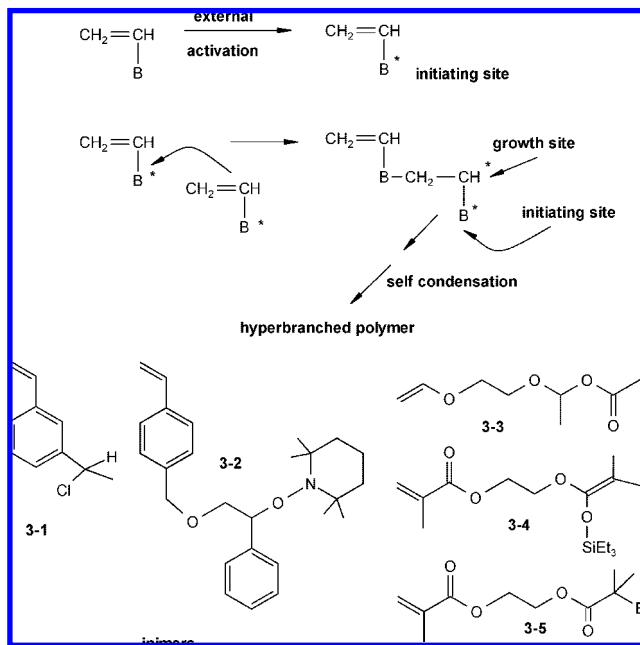
hyperbranched polyethers having poly(ethylene glycol) (PEG) segments at their molecular periphery were prepared by a simple procedure wherein an AB_2 type monomer (1-(6-hydroxyhexyloxy)-3,5-bis(methoxymethyl)-2,4,6-trimethylbenzene) was melt-polycondensed with an A-type monomer, namely, heptaethylene glycol monomethyl ether.[76] The presence of a large number of PEG units at the termini rendered a lower critical solution temperature (LCST) to these copolymers, above which they precipitated out of an aqueous solution. However, the addition of A-monofunctional compounds directly in the AB_x polyreaction is limited and usually low molar mass products result.

$A_2 + B_y$ **and Related Approaches.** The $A_2 + B_y$ approach differs strongly from the classical AB_2 approach, where gelation can never be reached under the Flory prerequisites, and actually, it has been questioned whether the resulting products can be termed as "hyperbranched". Highly branched structures similar to hyperbranched materials are usually reached on the way toward networks just before the critical conversion (gel point) is reached. This classical network formation approach, where A_2 and B_2 monomers are combined with B_y, has been known for a long time and has high technical relevance with a broad portfolio of suitable structures.[25] Gelation theories apply also for $A_2 + B_y$ systems,[77] but early on, for practical considerations, the critical molar ratio of A/B groups was defined as the limiting molar ratio at which gelation took place at full conversion of the minority groups. Below this molar ratio or at lower conversion, the gel point could not be reached and only soluble branched polymers were formed.[78] In the late 1990s, several research studies began to use a combination of commercially available A_2 and B_y ($y \geq 3$) monomers and explored this approach as a feasible alternative[29,28,79,80] to the Flory approach, which relies on specifically designed and synthesized AB_x monomers that are not commercially available (Scheme 2). Thus, hyperbranched aromatic polyamides[79] and polyethers[29] have been obtained using combinations of suitable $A_2 + B_3$ monomers when the reaction was stopped prior to the gel point. However, the gel formation in these

condensations is dependent on many factors, e.g., the ratio of functionalities, monomer concentrations, purity of solvent and reagents, reaction time and temperature, and others,[81] and therefore, it is very difficult to fully control the reaction and to obtain hyperbranched polymers with high molar mass without the need for separation of the sol from the resulting gel fraction. In addition, the growth and structure as well as the property profile of the $A_2 + B_y$ products are not fully comparable to that of AB_x polymers.[81] The structural variety is higher, since more variations regarding linear and branched units exist and certainly, the resulting polymer structures contain B as well as A functions in a significant amount, which depends on the ratio of A_2 to B_y in the monomer mixture.[81–83] For achieving reasonable molar masses as well as avoiding premature gelation, a functionality ratio A/B of 2:3 with functionality conversion below 87% provides generally favorable reaction conditions.[25,84] If a functionality ratio $A/B = 1:2$ is chosen, the system resembles an AB_2 approach with no danger of cross-linking. However, due to the high stoichiometric imbalance, only low molar mass products result when two different monomers are used. In the $A_2 + B_3$ approach, it is that rather easy to reach a degree of branching above 50%, e.g., at A/B ratio 1:1 or when the monomers are added stepwise.[84,85] The resulting macromolecules, which contain several nonreacted A functional groups, make the $A_2 + B_y$ hb products susceptible to postpolymerization reactions that can easily result in gelation. Recently it was found that postcondensation in the melt processing renders $A_2 + B_3$ aromatic polymers much less suitable as processing aids than AB_2 polyesters.[86] A detailed comparison of the AB_x and the $A_2 + B_y$ approach has been outlined by Kricheldorf,[87] pointing to differences in the kinetic pathways for the polymerizations. Of significant importance for the resulting structure as well as further reactivity is the question of whether the polycondensation reaction employed in the $A_2 + B_y$ approach is kinetically controlled (irreversible) or thermodynamically controlled (reversible). Cyclization tendencies in reversible as well as irreversible reactions will help to avoid gelation,[87,88] as will steric hindrance, which reduces the degree of branching.[89]

There have been a variety of attempts to improve the $A_2 + B_3$ approach by using monomers with a selectively higher reactivity of one A or B ($AA' + B_y$ or $A_2 + B'B_x$) or even of an A and a B function ($AA' + B'B_x$), favoring the formation of an $A(A' - B')B_x$ intermediate from easily available monomers. Several examples have been reported already in the literature in this regard.[90–94] A comprehensive review on the various approaches as $A_2 + BB_2'$, $A_2 + CB_y$, $AB + CD_y/C_y$, $A* + CB_2/B_y$, $AA* + B_2$, or $A_2 + B_2 + BB_2'$, where B or C reacts faster or more easily with A than D or B', is given in the review by Gao and Yan.[5] One prominent example is the formation of hyperbranched poly(urea urethane)s from an A_2 (or AA') $+ CB_2$ system as reported by Bruchmann et al.[17,19,95,96] and also at the same time by Yan et al. (Scheme 2).[97] Here, the final structure contains both urea and urethane groups and both exist in linear, terminal, and dendritic units (see section 2.2.7). Nevertheless, even in this very complicated structure, NMR spectroscopy proved to be a very powerful tool, and a complete structure analysis was possible with verifying a DB significantly above 50% (between 60 and 70%).[98] As a general feature, because of the unequal reactivity of the functionalities, often degrees of branching above 50% are achieved in the $A_2 + CB_2$ and related approaches.[5] However, even though the formation

Scheme 3. Mechanism of Self-Condensing Vinyl Polymerization According to Fréchet[30] and Some Examples of $AB*$ Inimers
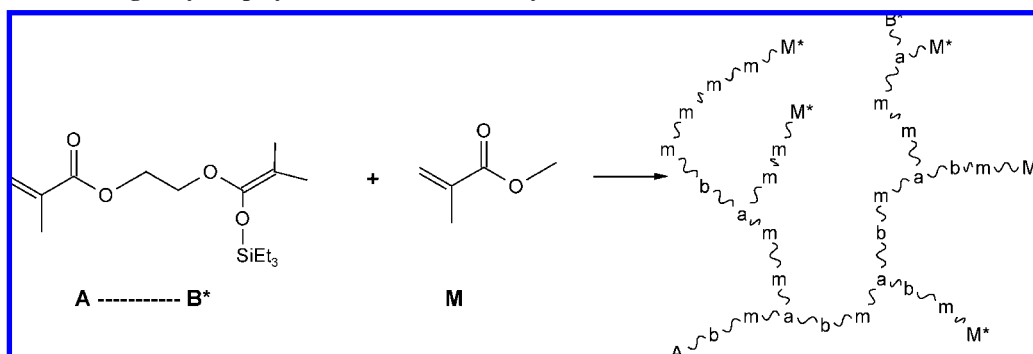

of the expected AB_x intermediate can be verified, these various approaches do not fully avoid the problem of gelation.

Other structures cover poly(amine ester)s through $AB + CD_2$,[99] poly(amido amine)s through $AB + C_n$,[100] as well as poly(sulfone amine)s[101] and poly(ester amine)s[102] through $A_2 + BB_2'$ using addition reactions of amines (Scheme 2). One industrial example is the hyperbranched poly(esteramide) (Hybrane) with alcoholic end groups developed by DSM from AB_2 monomers in situ formed from different anhydrides and diethanolamine ($A* + CB_2$, Scheme 2).[9,103] The polycondensation proceeds when a slight excess of diethanolamine is added without any catalyst at 140 °C. The material properties, especially the glass-transition temperature, are controlled by the used anhydrides and by end group modification.[9]

2.1.2. Chain-Growth Approaches

The use of chain-growth mechanisms in the preparation of highly branched polymers has rapidly increased since self-condensing vinyl polymerization (SCVP) was initially reported by Frechét et al.[30] in 1995 for the synthesis of hyperbranched polymers (Scheme 3). Chain-growth mechanisms are employed in SCVP, in self-condensing ring-opening polymerization SCROP (also known as ring-opening multibranching polymerization = ROMBP), or in proton transfer polymerizations,[34,48] as well as various copolymerizations.[32] Newer approaches use monomers and cross-linkers in the presence of transfer agents or, e.g., functionalized 1,1-diphenylethylene derivatives in combination with anionic polymerization.[104] Associated with these chemistries are the various dendrigraft approaches and dendrimer-like polymers,[3,40,105] which usually also rely on chain-growth reactions but are characterized by linear segments between the branching points. These concepts will be discussed in a separate section (section 2.3.2).

Self-Condensing Vinyl Polymerization. Self-condensing vinyl polymerization (SCVP) is based on a vinyl monomer that additionally bears an initiating group ("inimer" =
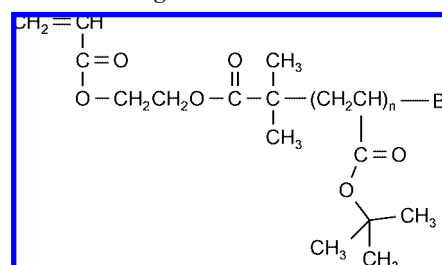
Scheme 4. Self-Condensing Vinyl Copolymerization As Shown by Müller et al.[121]

Scheme 5. *AB** Macroinimer for the Preparation of Highly Branched P*t*BuA through ATRP[124]

initiator + monomer[106]). These monomers allow propagation through the double bond (=chain growth) and addition of the initiating site to the double bond (=step growth) and thus lead to hyperbranched polymers in a one-pot reaction with possible branching in each repeating unit and, thus, with the potential to reach a degree of branching of 50% (Scheme 3). The inimer route to hb polymers was likely first observed by Nuyken et al.[107] in the living cationic copolymerization of 4-(chloromethyl)styrene and isobutylene since a significant number of branch points were formed in the macromolecules, which were initially intended to be linear macroinitiators. The living cationic polymerization of 3-(1-chloroethyl)ethenylbenzene (**3−1**) at low temperature using SnCl$_4$ was also the basis for the first intentional successful synthesis of hyperbranched polymers.[30] Polymers with low Kuhn−Mark−Houwink−Sakurada constants were achieved as typical for globular structures.

This process has been readily extended using other controlled chain-growth processes, especially group-transfer polymerization[108,109] and controlled radical polymerizations like nitroxide-mediated radical polymerization (NMRP) (**3−2**),[110] atom-transfer radical polymerization (**3−5**),[111−113] and reversible addition−fragmentation chain transfer (RAFT)[114] (see also Scheme 21, **21−3**, and Scheme 37), as well as ruthenium-catalyzed coordinative polymerization.[115] Some suitable inimers are highlighted in Scheme 3. Hyperbranched polymethacrylates were prepared by means of *oxyanionic vinyl polymerization* of commercially available monomers like hydroxyethyl methacrylate as inimer.[116]

A general feature of SCVP is the unequal reactivity between chain growth of the vinyl group and step growth through the initiating site. Therefore, the degree of branching DB can differ strongly from the value 50% of the random *AB*$_2$ condensation and depends on the reactivity ratio of the *A** or *B** end groups. Frechét[111] demonstrated that, just by varying the reaction conditions, the DB achieved in the metal-catalyzed "living" radical polymerization of 3-(1-chloroethyl)ethenylbenzene **3−1** can be varied from nearly zero (linear polymer) to highly branched. The danger of side-reactions (elimination, radical coupling) limits also the use of controlled radical processes. At longer reaction times, in particular, gel fractions cannot be avoided.
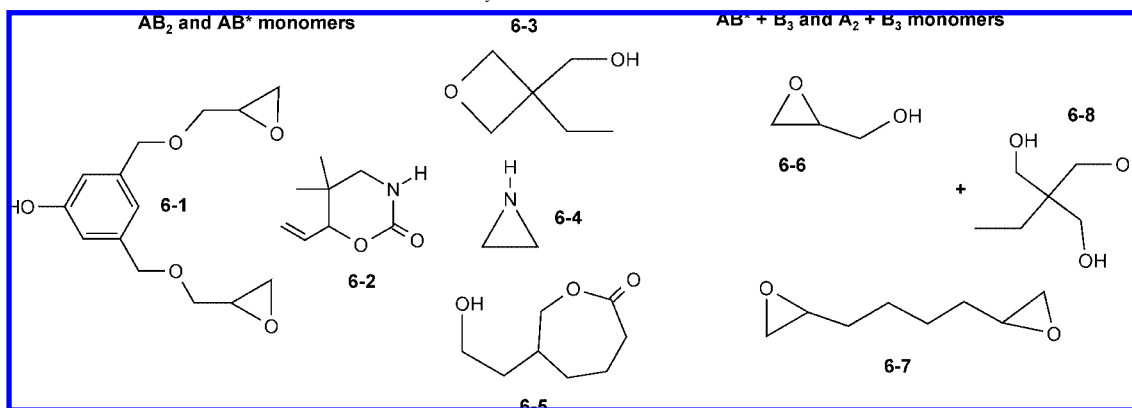
Often in SCVP it is not possible to determine the DB directly via NMR analysis. Therefore, indirect methods, e.g., viscosity measurements and light-scattering methods selective toward the more globular structure of a hyperbranched polymer, have to be used to indicate the branched architecture. The polydispersity is usually very high and represents the presumably nonliving character of the reaction. However, the big advantage is the extension of the concept of

hyperbranched polymers to vinyl monomers and chain-growth processes, which opens unexpected possibilities for new materials. Thus, the mechanism and kinetics[117] of SCVP, the molar mass and polydispersity development with conversion,[106] the degree of branching,[118] the influence of a core molecule (meaning a multifunctional initiator),[119] and the effect of different reaction rate constants[120] have received extensive theoretical treatment.

SCVP can readily be carried out as a copolymerization with conventional monomers, which is an easy way to prepare highly branched and high molar mass polymer architectures (Scheme 4).[32,121−123] In the copolymerization, the molar mass distribution is reduced compared to the inimer homopolymerization, and the degree of branching can be adjusted to the desired property profiles, as will be addressed also in section 2.3.1. "Macroinimers",[124] a term coined by Hazer,[125] are macromonomers possessing an initiating site (Scheme 5), which can also lead to highly branched polymers.

Ring-Opening Multibranching Polymerization. ROMBP or self-condensing ring-opening polymerization (SCROP) differs from SCVP in the fact that instead of a vinyl group a heterocyclic group is used as the monomer part of the inimer. In addition, whereas in SCVP usually irreversible reactions are involved, in ROMBP also reversible preconditions generally have to be considered. The ROMBP approaches have their origin in classical ring-opening reaction mechanism (ROP) toward linear polymers, especially polyethers and polyesters. Chang and Fréchet[126] reacted a diepoxy-substituted phenol (**6−1**, Scheme 6) involving a proton-transfer mechanism to a hb polymer. In the first step of the polyreaction, a proton is abstracted from the phenol group by an OH$^-$ to yield the phenolate. The nucleophile phenolate then adds to a second molecule 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 a nonreacted monomer, yielding again the phenolate, which reacts as nucleophile. An important feature, in order to achieve this type of growth

Scheme 6. AB_2 and $AB*$ Monomers As Well As $A_2 + B_y$ Monomer Combination for ROMBP

without undesired propagation through the nucleophilic center of the secondary alkoxide, is that the phenolate formation is significantly faster than the nucleophilic-propagation step. The much lower pK_a ($pK_a \approx 10$) of the phenolic group relative to that of the secondary alkoxide obtained by epoxide ring-opening ($pK_a \approx 17$) enables the fast proton exchange. Interestingly, the molar mass still increases exponentially with conversion as observed for the classical hyperbranched polycondensations.[77,127,128] 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 which was addressed generally for all hyperbranched polymers by Dušek et al.[67]

Commercial poly(ethyleneimine)[129] prepared by self-condensing ring-opening reaction of aziridine (**6**−**4**) is a branched polymer due to further reaction of the NH groups in the formed polymer chain with the cyclic monomer.

Describing the same principle, nearly at the same time, Penczek et al.[130] and Hult et al.[131] published the successful cationic ring-opening polymerization of 3-ethyl-3-(hydroxymethyl)oxetane (**6**−**3**) leading to hyperbranched aliphatic polyethers with a degree of branching in the range of 41% and molar masses $\bar{M}_n$ around 2 000−5 000 g/mol. Benzyltetramethylenesulfonium hexafluoroantimonate, $BF_3O(C_2H_5)_2$, or CF_3SO_3H have been applied as initiators and trimethylolpropane was added as the 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).[130] However, in addition, two hydroxymethylene functions can be condensed under acid catalysis, forming an ether bond (activated monomer mechanism), 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 co-workers[132] published the formation of hyperbranched polyesters based on 5-(2-hydroxyethyl)-ε-caprolactone (**6**−**5**, Scheme 6). The monomer, similar as all cyclic monomers used in ROMBP, looks first like an AB monomer and changes to an AB_2 type after the first addition of a second monomer (*latent AB_2* monomer). The propagation and initiation proceed entirely through one type of reactive nucleophile: a primary alcohol. Bulk polymerization of **6**−**5** in the presence of stannous octoate as catalyst yielded

hyperbranched polymers of $\bar{M}_w = 65\,000-85\,000$ g/mol ($\bar{M}_w/\bar{M}_n = 3.2$) and a DB of 50%, indicating equal reactivity of both primary alcohol groups.
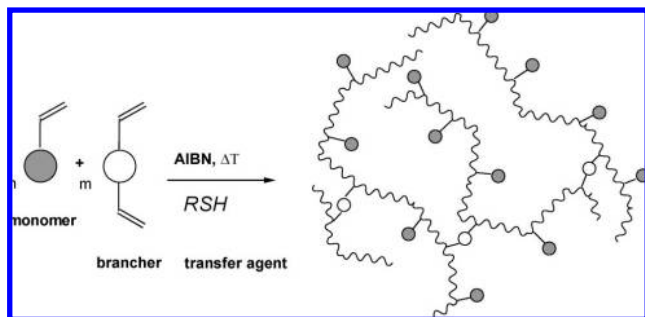
It has been also known for some time that the cationic polyreaction of glycidol **6**−**6** results in branched polymers.[133,134] Frey et al.[135] described the anionic polymerization of glycidol, which they consider also as a latent AB_2 monomer. The polymerization proved to be very versatile and leads to hyperbranched polymers with rather narrow molar mass distribution ($\bar{M}_w/\bar{M}_n = 1.1-1.4$) due to a chain-growth-like character of the reaction when only partial deprotonation to the initiating alkoxide (initiating site), e.g., the triol **6**−**8**, was performed. This leads to a more or less simultaneous growth of all chain ends and allows the control of molar mass and polydispersity. After deprotonation of **6**−**8**, the resulting alkoxide reacts with the nonsubstituted end of **6**−**6** and thereby generates a secondary alkoxide. In contrast to the cationic polymerization of glycidol described by Penczek and Dworak,[134] 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 were controlled. The degree of branching was determined to be 53−59%, which is somewhat lower than expected theoretically for the slow monomer approach (67%).[73]

In this respect, it should be mentioned that a very interesting approach toward hyperbranched polyamines based on a cyclic carbamate using a multibranching polymerization-type ring-opening reaction had been published by Suzuki et al.[31] early in 1992. The approach was further extended toward **6**−**2** in 1998.[136] In this case, the monomer has no resemblance to any ABB' or AB_2 monomer discussed up to now. Growth occurs only when an initiator with an active B group is added together with a catalyst.

Transfer Concepts and Other Chain-Growth Mechanisms. Various chain-transfer concepts have also been employed for the synthesis of hb polymers. One is the use of so-called "iniferter", monomers which contain a chain-transfer group like methacrylate and styrene derivatives with thiocarbamate groups (see also Scheme 37)[137,138] or a dithioester group.[114] Nuyken and Wieland[139] developed a concept to use an azomethylmalonodinitrile substituted styrene derivative for the preparation of highly branched polymers via a radical process. The dithiocarbamate or malonodinitrile fragments achieved during UV radiation or thermal decomposition act as reversible termination/transfer agents but not as initiators, and therefore, cross-linking reactions can be avoided even in the nonliving systems. Related is the use of a styrene

Scheme 7. Highly Branched Polymers through Free Radical Polymerization Using Branching Monomers in Combination with Significant Amounts of Transfer Agents (RSH)[142]
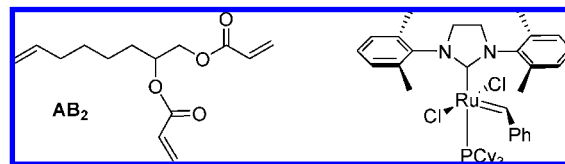

Scheme 8. AB_2 Monomer and the Used Metathesis Catalyst Used for the Synthesis of hb Poly(ester−ene)s through ADMET as Described by Grubbs and Co-workers[155]

derivative in anionic polymerization that contains a chlorodimethylsilyl substituent that undergoes quantitative S_N2 reactions. This system requires a slow monomer addition process to avoid gelation.[140] Branching can also easily be introduced, leading to a variety of highly branched polymer architectures like star-branched and dendritic-branched, when suitable bromo- or chloro-functionalized 1,1-diphenylethylene derivatives are employed in living anionic polymerization in combination with conventional monomers.[104,141]

Controlled transfer reactions are also the reason why soluble polymers are obtained in the free radical polymerization of monomers in the presence of cross-linkers (bifunctional monomers like bismethacrylates). Here, large amounts of chain-transfer agents are added to avoid gelation (Scheme 7), but the resulting products exhibit extremely broad molar mass distributions and very multimodal size-exclusion chromatography (SEC) traces and the transfer agents, e.g., alkanethiols (RSH), are incorporated into the macromolecules as end groups.[142−145] Similarly, hyperbranched poly(methacrylates) were prepared by RAFT polymerization of MMA and ethylene glycol dimethacrylate as a branching agent, mediated by the RAFT agent 2-(2-cyanopropyl) dithiobenzoate.[146] Hyperbranched poly(divinylbenzene)s from divinylbenzene (DVB) and 1,3-diisopropenylbenzene by anionic SCVP are reported by Baskaran,[147] and Gong et al.[148] used ATRP of divinylbenzene in combination with the initiator (1-bromoethyl)benzene and also achieved soluble hb products. Similarly, Wang et al.[149] prepared, through deactivation-enhanced ATRP, novel dendritic poly(DVB) and poly(EGDMA) (ethylene glycol dimethoylate = EGDMA) polymers from homopolymerizations of commercially available multifunctional vinyl monomers. No cross-linking or microgel was observed in the polymer provided that the overall monomer conversion was kept below 60%. Armes et al. published similar results for the ATRP of EGDMA with bisphenol A dimethacrylate as branching agent.[150] It was found that, only at low EGDMA content (less than one branching agent per primary chain), gelation could be avoided and branching occurred only at high monomer conversion (>90%).

Brookhart et al.[151] and then Guan et al.[152] 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 (see Scheme 44). Even higher branching was observed by Sen et al.[153] with a [Ni(π-methallyl)(Br)]₂ 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 previously by Fink and co-workers[154] in 1985 for α-olefins.
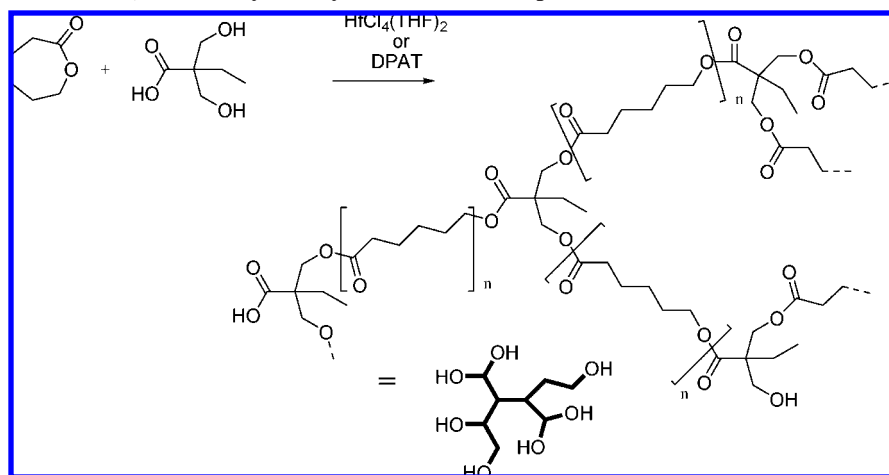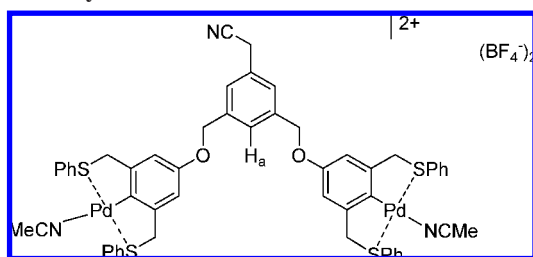
The Brookhart discoveries show that the polyethylene topology can be well-controlled from nearly linear to hyperbranched just by the reaction pressure, which in principle is similar to the long-chain branching introduced in low-density polyethylene by transfer reactions. The change in topology could be verified by differences in hydrodynamic radius and solution viscosity for samples prepared at different pressures but with similar $\bar{M}_w$ as determined by multi-angle laser light scattering (MALLS).[152]

Another example of a chain-transfer process is the work of Grubbs et al.[155] Grubbs used acyclic diene metathesis polymerization (ADMET) under mild reaction conditions (40 °C) of simple AB_2 monomers for the preparation of hyperbranched poly(ester ene)s with acrylate end groups (Scheme 8). The used imidazolinylidene-based catalyst is tolerant to many functional groups, is stable to air and moisture, and readily promotes cross-metathesis between electron-rich primary olefins. When treated with this catalyst, electron-poor olefins do not homodimerize but do participate in a secondary metathesis reaction with homodimers of more reactive olefins. Therefore, any molecule functionalized with one electron-rich olefin, such as a terminal alkene, and two or more electron-poor olefins, such as acrylates, is an AB_x-type monomer (Scheme 8) that can be polymerized without any gelation.

2.1.3. Other Synthetic Approaches

The above-described synthetic approaches cover most general methods to prepare hyperbranched or related highly branched structures. However, in order to further increase the structural variety and complexity of the designed macromolecular structures, increasingly, combinations of highly branched structures with linear units are described that lead to linear−dendritic block-copolymers, dendronized polymers, hb-core-star structures, dendrigrafts, and further complex architectures. Copolymerization of AB monomers with AB_x monomers was described as early as by Flory[77] and has been used for commercial products,[5] but intentional "dilution" of the branching in hyperbranched polymers and the design of complex architectures are newer aspects of this concept. Some of these structures will be outlined in more detail in section 2.3. Frey et al. combined, e.g., the step-growth AB_2 approach with chain-growth ROMBP in one-pot reactions from ε-caprolactone and 2,2-bis(hydroxylmethyl) butyric acid (Scheme 9).[156]

Noncovalent bonding and self-assembly can also be used to prepare hb polymers. For example, a hyperbranched polymer based on the reversible self-assembly of an organopalladium methylcyano complex has been reported by Reinhoudt et al.,[157] and it can be "degraded" to the monomer by addition of acetonitrile (Scheme 10). A variety of self-assembly concepts, often used for the preparation of well-defined dendrimers but especially for the preparation of larger nanocapsules, are summarized by Smith et al.[158]

Scheme 9. Copolymerization of 2,2-Bis(methylol)butyric Acid with ε-Caprolactone via ROMBP[156]

Scheme 10. AB_2 **Monomer As Described by Reinhoudt for the Preparation of hb Polymers through Noncovalent Bonds; Nanoscale Capsules Were Obtained through Reversible Self-Assembly[157]**

2.2. Examples of hb Polymers Classified by Reactions and Chemistry

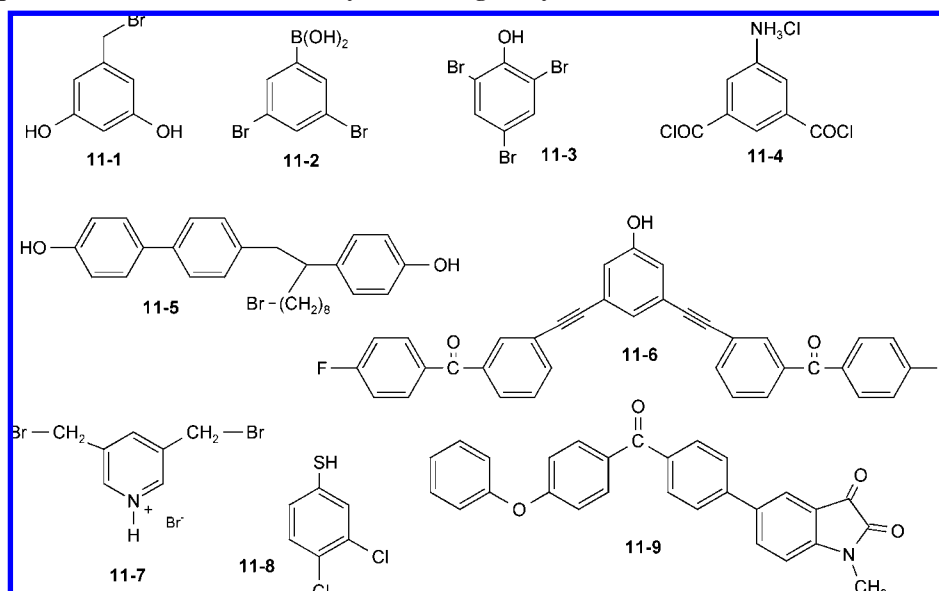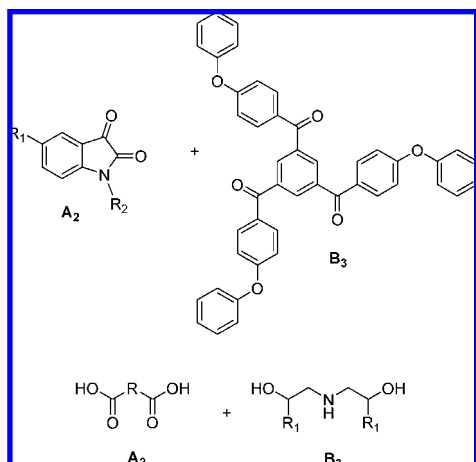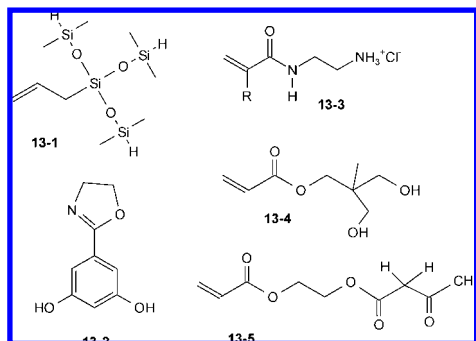### 2.2.1. hb Polymers through Polycondensation

Polycondensation is the classical way to prepare hyperbranched polymers by AB_x monomers with and without core moieties. This starts with the early work on an aromatic polyether by Hunter[45] (through **11−3**, Scheme 11) and polyesters reported in a patent,[60] but accounts also for the C−C coupling reaction toward polyphenylenes where the term hyperbranched was introduced by Kim and Webster (through **11−2**).[59] As already mentioned earlier, especially polyester structures had been favored early on by many groups[15,60−65,65] and also industry (Boltorn based on bismethylolpropionic acid) due to the availability of suitable monomers. Because of this high importance, a separate chapter will be devoted to highly branched polyesters. Almost all classes of condensation polymers have been adopted for hb polymer synthesis, e.g., polyamides (e.g., through **11−4**),[159−163] polyethers (e.g., through **11−1, 11−5**),[68,164−166] polyethersulfones and -ketones (e.g., through **11−6**),[167−171] polyphenylenesulfides (**11−8**),[172] polyaryleneether,[173] polyphenyleneoxide,[174] polycarbonates,[175] polyphenyl acetylenes,[176] polysiloxanes[177] and various other structures like poly(bis-(alkylene) pyridinium)s[178] (**11−7**) and poly(arylene oxindole)s[179] (**11−9**), and were readily synthesized through condensation reactions. Some selected AB_2 monomers used are shown in Scheme 11. Polycondensations are often carried out in bulk, but solution polymerizations are also suitable and often prevent side reactions. As required for all polycondensates, the low molar mass condensation products need to be removed, e.g., by applying vacuum in melt polycondensation in order to drive the reactions to high conversions.

Internal cyclization, as observed to a significant extent in the melt polycondensation of bismethylolpropionic acid without adding a core molecule, may further limit the molar mass buildup. As many polycondensates are prepared by equilibrium reactions, it is difficult by this approach to prepare complex architectures with differences in branching density, since at high temperatures an equilibrium state will be reached.

Increasingly, hb polycondensates are synthesized also by the $A_2 + B_y$ approach from easily available monomers (Schemes 2 and 12). Thus, hyperbranched polyaramides,[79,82] polyimides,[8] polyesters,[20,180] polyesteramides,[9,181] polycarbonates,[182] polyethers,[29,183] poly-Schiff-base,[184] polyarylamine−phenylene,[185] polyphenylenevinylene,[186] triazine based polyamines,[187] and other structures like polyphenyloxindazole[188] have been reported. For the latter, Smet et al.[188] developed a facile approach to hyperbranched polymers by applying a super-electrophilic reaction based on an $A_2 + B_3$ strategy using isatins and a trifunctional aryletherketone (Scheme 12). A significant reactivity difference between the intermediate and the starting material was utilized to avoid gelation in the $A_2 + B_3$ polymerization. Li et al.[181,189] modified the $A^* + CB_2$ approach (A^* = anhydride ring structure) as developed by DSM for Hybrane (polyesteramide)[9] to a $A_2 + CB_2$ approach using a diacid instead of an anhydride (Scheme 12), which leads to a lower tendency for selective AB_2 intermediate formation; thus, the reaction conditions at the beginning of the polymerization had to be carefully controlled. Kou et al.[190] added to a core moiety under slow monomer addition conditions an AB_2 compound achieved from the $A^* + CB_2$ molecules employed usually in Hybrane synthesis and obtained products that were readily further modified at the OH end groups.

2.2.2. hb Polymers through Addition Step-Growth Reactions

Polyaddition processes, step-growth polymerizations without the elimination of small molecules, have, likewise, been employed for the preparation of hb polymer. The most important examples are based on polyurethanes and polyureas.[19,191−193] Because of the ongoing strong interest in these types of hb polymers, a separate chapter is devoted to hb polyurethanes, polyurea urethanes, and polyureas, which are prepared directly through AB_x or $A_2 + B_y$ approaches or which are built up through the use of hb polyalcohols or polyamines in PU coating and resin formula-

Scheme 11. Examples of AB_x Monomers for hb Polymers through Polycondensation

Scheme 12. $A_2 + B_3$ Monomer Combinations for the Preparation of hb Poly(phenyloxindazole) and Poly(esteramide)

Scheme 13. AB_x Monomers for the Preparation of hb Polymers through Polyaddition Reactions
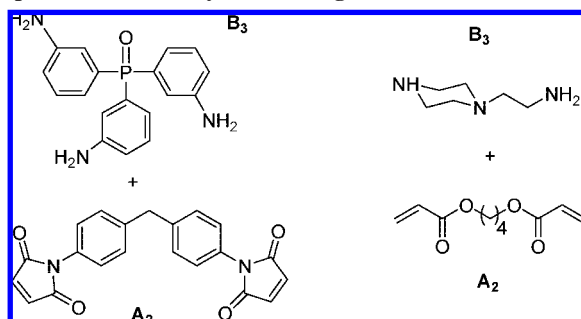

tions (section 2.2.7). Polyaddition reactions, e.g., of AB_3 monomer **13−1** (Scheme 13), are also used for polycarbosilanes[54,56,177,194−197] involving the classical hydrosilylation reaction.

Hyperbranched poly(etheramide)s, without encountering any side reactions, were prepared via nucleophilic ring-opening addition reaction of phenols on oxazolines[198] using the AB_2 monomer 2-(3,5-dihydroxyphenyl)-1,3-oxazoline

13−2.[199] The thermally induced reaction proceeds in *N*-methylcaprolactam solution above 190 °C. The products are randomly branched with a degree of branching of 50%, which was verified by high-resolution NMR studies.

Michael addition reactions are ideal for dendrimer synthesis due to the low probability of side reactions and the mild reaction conditions, and thus, the two most prominent dendrimers were prepared through that approach.[50] Dendritic poly(amidoamine)s, PAMAMs, were synthesized through the addition of methylacrylate to amine substrates like ammonia and diethylene amine by Tomalia.[200] Polypropylene imines (PPI),[201] the second-most well-known dendrimer, which had been commercialized under the trade name Astramol,[202] are accessed through the Michael addition of primary diamines with acrylonitrile followed by hydrogenation of the nitrile groups to amines and repeated reaction with acrylonitrile. The Michael addition reactions were quickly adapted to the synthesis of hyperbranched structures. The recent advances in the use of Michael addition step-growth reaction for linear polymers, network formation, and dendritic polymers have been excellently reviewed by Long et al.[203] For example, Hobson and Feast[204] used a high-temperature Michael addition reaction of the AB_2 molecule **13−3**, which leads to a hyperbranched polymer nearly identical to the PAMAM dendrimers of Tomalia.[200] Surprisingly, the authors reported for the resulting hyperbranched poly(amidoamine)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 steric or thermodynamic factors involved in the reaction.

An $A_2 + B_3$ methodology was reported in the synthesis of thermally stable high T_g poly(aspartamide)s with amino end groups from bismaleimides and aromatic triamines (Scheme 14).[205] Michael addition reactions involving amines are specially favored, as was also shown in the various $A_2 + B_y$ variations summarized by Gao and Yan.[5] This involves the above-mentioned poly(sulfone amine)s[101] by $A_2 + BB'_2$ reaction of divinylsulfone and (1-aminoethyl)piperazine (Scheme 2) as well as various poly(ester amine)s, again obtained through reaction of $A_2 + B_3$ monomers with unequal reactivity (e.g., ethylene or butylenes diacrylate + (1-

Scheme 14. $A_2 + B_3$ Monomer Combinations for the Preparation of hb Polymers through Michael Addition

Scheme 15. Cycloaddition Reactions Used for the Buildup of hb Polymers

aminoethyl) piperazine)[102,206,207] or equal reactivity (e.g., piperazine and trimethylolpropane).[208] The level of the substitution at the amines in B_y as well as the stoichiometric ratio of the two components A_2 and B_y controlled the final degree of branching.

Highly branched poly(ether amine)s were prepared by the addition reaction of the amino end functions of the commercially available highly branched polyethylene imine (PEI) with PEG diacrylates. The ester groups in the resulting polymer structure allowed easy biodegradation, and the materials showed high efficiency in gene transfection due to complex formation with DNA.[209]
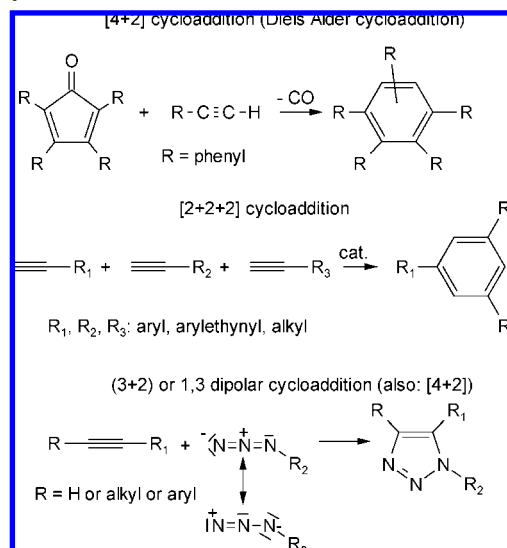
Other compounds in addition to amines have been studied in Michael addition. Thus, Endo et al.[210] reacted hydroxyethylacrylate with a diketene by acetoacetylation. The resulting AB_2 monomer **13−5** was converted into a hb polyester with acetylacetate end groups in the presence of a base like diaza (1,3) bicyclo [5.4.0] undercane (DBU). Again, relatively high degrees of branching of up to 83% were reported since the monoadduct exhibits higher reactivity toward the acrylate group than the original acetoacetate group. A similar chemistry was used in the $A_2 + B_4$ approach by Trumbo,[211] who reacted diacrylates with bisacetoacetates. Here, gelation was avoided when excess of bisacetoacetate was used, and high molar mass products ($M_w > 400\,000$ g/mol) with broad molar mass distributions (>10) were reported.

Kakodawa et al.[212] studied the self-condensation of 2,2-bis(hydroxymethyl)propyl acrylate **13−4** initiated by triphenylphosphine leading to low molar mass poly(ether ester)s containing phosphonium ions. Hyperbranched polyphosphate acrylates, which can be used for UV-curable flame-retardant coatings, were also prepared by the $A_2 + B_3$ polyaddition reaction of tri(acryloyloxyethyl) phosphate with piperazine by Huang and Shi.[213]

2.2.3. hb Polymers through Cycloaddition Reactions

Cycloaddition reactions are assuming an increasingly important role in the synthesis of hyperbranched polymers. They permit excellent control of the reactions with high selectivity and good yields. The reactions are usually carried out under mild reaction conditions tolerating functionality and allow for the creation of entirely new polymeric structures.[3,14,214] Principally the [2 + 2 + 2], the Diels−Alder [2 + 4], and the [3 + 2] or 1,3-dipolar cycloaddition reactions have been applied for dendritic structure synthesis. 1,3-Dipolar cycloaddition reactions are dominated by the click reaction of azides and alkynes (Scheme 15).

In general, polyphenylenes possess high thermal and chemical stability. However, in contrast to their linear
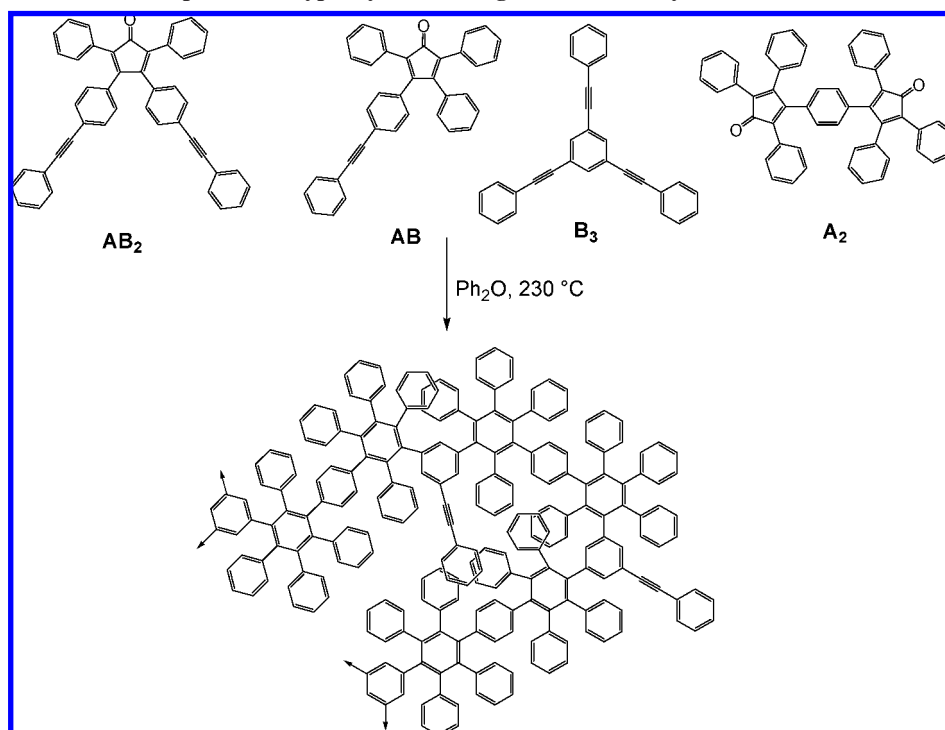
analogues, the hyperbranched polyphenylenes are nonconducting polymers, because an extended π-conjugation is hindered due to their tightly packed and strongly twisted phenylene units.[215] They show good solubility and processability comparable to those of the corresponding dendrimers[216] and are more easily available in larger quantities. Because of the outlined properties, hyperbranched polyphenylenes are promising candidates for the application as insulating materials in microelectronics, where features like high thermal stability, good processability and solubility, and low moisture absorption are required.[217] An example for a low-dielectric-constant polymer based on branched and cross-linked polyarylenes that has been explored by the semiconductor industry is SiLK from The Dow Chemical Company.[218] In addition, suitably modified AB_2 monomers could be polymerized in nanochannels to hb polyphenylenes nanotubes, which could be transformed into porous carbon nanochannels.[219]

The first hyperbranched polyphenylenes through AB_x were synthesized by Kim and Webster through *C,C*-coupling starting from (3,5-dibromophenyl)boronic acid (**11−2**) and dihalophenyl Grignard reagents via Pd(0)- and Ni(II)-catalyzed aryl−aryl coupling reactions, respectively.[51] Müllen et al.[220,221] reported the Diels−Alder reaction of the AB_2 monomers 3,4-bis-(4-(tri-isopropylsilylethynyl)phenyl)-2,5-diphenylcyclopentadienone or 3,4-bis-(4-(phenylethynyl)phenyl)-2,5-diphenylcyclopentadienone (Scheme 16). Depending on the substitution on the ethynyl group, thermal treatment at 180 °C, with or without the presence of tetrabutylammonium fluoride, for up to 45 h is necessary to afford the hyperbranched products with molar masses $\bar{M}_w$ up to 100 000 g/mol and broad polydispersity.[220]

This approach has been extended recently by combining the AB_2 monomer 3,4-bis-(4-(phenylethynyl)phenyl)-2,5-diphenylcyclopentadienone with an AB monomer; the reaction was carried out in diphenylether at 230 °C (Scheme 16). Besides giving some control over the degree of branching in the branched polyphenylenes, the addition of the AB monomer, e.g., in a 3:1 (AB_2/AB) ratio, limited the achievable molar masses to some extent: $\bar{M}_w$ values of up to 75 000 g/mol were obtained compared to up to 600 000 g/mol for pure AB_2 monomer used under identical reaction conditions.[89]

Scheme 16. Monomers Used to Prepare hb Polyphenylenes through Diels Adler Cycloaddition

Harrison and Feast[222] reported the preparation of highly soluble hyperbranched polyarylimides also using the Diels−Alder cycloaddition reaction but employing AB_2 monomers with maleimide and cyclopentadienone moieties. They also react upon heating in a suitable solvent like nitrobenzene in a [4 + 2]-cycloaddition reaction, forming a cyclohexadiene dicarboxylic acid imide, which could be further oxidized to a benzimide unit.

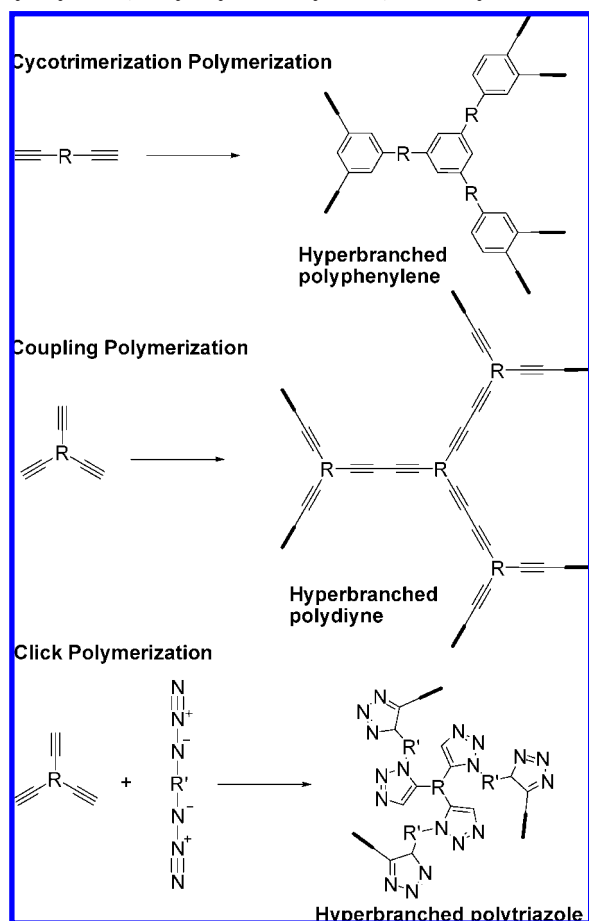Fully soluble hyperbranched polyphenylenes via the Diels−Alder reaction have been prepared also by the A_2 + B_3 approach[89] following the route demonstrated by Müllen et al.[215] (Scheme 16). It is interesting to note that, with this monomer combination, higher steric hindrance was achieved in the final polymer structures as compared to the hyperbranched polyphenylenes prepared by the AB_2 monomers. Thus, detailed NMR investigations[83] revealed that the formation of linear units is favored since the reactivity of the third B unit in B_3 is reduced after two B's have already reacted. Only when high excess of A_2 is used does the formation of dendritic units become more significant; however, the achievable molar mass is limited. An advantage of this reaction is that the critical conversion is changed by this reduced reactivity and, therefore, only fully soluble products were obtained under the conditions that were applied.

As previously mentioned, Korshak reported in the early 1970s the synthesis of branched polyphenylenes through cyclotrimerization of various diethynylbenzene with phenylacetylenes.[46] Linear and terminal units which accompany the cyclic dimers were considered as "anomalous" units in the soluble highly branched resin precursor polymers at that time.[46] Hyperbranched polyphenylenes and -arylenes can also be prepared by [2 + 2 + 2]-cycloaddition reactions as reported by Tang et al.[223−228] Here, the diyne polycyclotrimerization initiated by transition-metal catalysts[225,226] and base-catalyzed alkyne polycyclization is applied.[227,228] In the first case, a variety of bifunctional arylene ethynylene and monofunctional alkyne monomers were combined and

tantalum, niobium, or cobalt catalysts were used. In this approach, the addition of the monoalkyne avoids gelation and induces flexibility into the system, leading finally to soluble products. Because of the UV-irradiated cobalt catalysis, the polymerization results in a random mixture of 1,2,4- and 1,3,5-trisubstituted benzenes, which makes the hb structure very irregular. Thus, the final structural features of the highly branched products are very complex. The resulting materials, however, exhibit photoluminescence and optical limiting properties and are of interest for the preparation of novel light-emitting devices.

Furthermore, it was shown that the polycyclotrimerization of bis(aryl ethynyl ketones) can also be initiated simply by the base piperidine, which leads to the formation of hyperbranched poly(aryloxyarylene)s with perfect 1,3,5-regioregularity and a high degree of branching (from 78% to 100%) in high yields (up to 99%) and with molar masses $\bar{M}_w$ up to 30 000 g/mol.[227,228] Here, bis(aryleneacetylene)s linked by rather flexible units, e.g., $-O(CH_2)_{12}O-$, were employed, and the highest degree of branching was achieved in tetralin as proven by spectroscopic means by the disappearance of any remaining alkyne units. These polymers were fully soluble in common organic solvents, showed high photosensitivity, and were readily photo-cross-linked to give photoresist patterns with nanometer resolutions. The group of Tang recently reported a variety of different A_n monomers (diynes and triynes) for polycycloaddition leading to hb polyarylenes, polydiynes, and also polytriazoles using click chemistry of diacetylenes with diazides (Scheme 17).[224]

Whereas the above outlined Diels−Alder reactions and [2 + 2 + 2]-cyclotrimerization reactions are especially well-suited to prepare highly aromatic hydrocarbon structures that exhibit high shape-persistency and usually a more nonpolar character, the 1,3-dipolar cycloaddition reactions offer the possibility to prepare complex heterocycles and also to introduce polar functionalities. In addition, depending on the reaction mechanism and the reaction conditions, high stereocontrol is possible and the formation of specific interme-

Scheme 17. Cyclopolymerizations Towards hb Poly(arylene)s, Poly(aryleneacetylene)s, and Polytriazoles

without any linear units and, therefore, featuring a degree of branching of 100%. In the first reaction of the maleimide with one of the azine units, an unstable azomethine imine cyclic system is formed as a linear unit, which can only go forward by reacting with the second azine to form a stable tetracyclic system or go backward to the starting material. Since the linear units are not stable, they cannot be found in the final product and only bisazine terminal units as well as tetracyclic fully dendritic units were observed, leading to a formal DB of 100%. These structural features and, thus, the absence of any linear units could also be proven by detailed NMR analysis and by the use of model compounds despite the rather high number of isomers found in the tetracyclic systems.[238] Nevertheless, irregularly branched products of molar masses $\bar{M}_w$ up to 10 000 g/mol and polydispersities around 2.5 were isolated and certainly qualified as "hyperbranched". This result on very high DB is similar to the one reported for the regioselective cyclotrimerization as reported by Tang and co-workers[227] and Smet et al.,[179,239] who were also able to prepare hyperbranched polymers with a degree of branching of 100%. Smet, however, did not use a cycloaddition reaction but rather the acid-catalyzed condensation of isatin with aromatic compounds, which led to hyperbranched polyaryleneoxindoles.

The 1,3-dipolar cycloaddition (CA) reaction, "click chemistry", was explored very successfully in dendrimer synthesis and functionalization.[3,14,240,241] Here one should note that the thermal cycloaddition reaction allows only minimal control of the regiochemistry, and therefore, two regioisomers are formed via *syn-* and *anti*-approaches. However, when terminal alkynes are employed, Sharpless[229] and Tornoe[232] pointed out that the *anti*-regioisomer is formed solely using a copper-mediated CA reaction. Unfortunately, this stereocontrol cannot be achieved when internal triple bonds are involved in the reaction.

As one could predict, the 1,3-dipolar CA reaction of azides and alkynes has also been applied in the field of hyperbranched polymers. The synthesis of novel hyperbranched poly(1,2,3-triazole)s via 1,3-dipolar cycloaddition was successfully achieved with the AB_2 monomer 3,5-bis(propargyloxy) benzyl azide, having an azide group as *A*-unit and two terminal triple bonds as *B*-units (AB_2-bisalkyne) (**19−2**, Scheme 19).[242] The polymerization of the AB_2-bisalkyne was conducted either via thermal polymerization or under copper(I) catalysis. The latter leads to insoluble products under the chosen reaction conditions (room temperature), probably due to the very high molar masses achieved and maybe also due to the occurrence of side reactions. However, full stereocontrol of the formed triazole units was maintainedk and only 1,4-substituion in the triazole ring as well as a degree of branching of 50%, which is typical for a random and ideal AB_2 condensation, was confirmed by ^{1}H and ^{13}C by (HR-MAS) NMR spectroscopy of the swollen samples. By autopolymerization at room temperature, fully soluble products of high molecular weight could be obtained from the AB_2-bisalkyne, but the regioselectivity was lost. The 1,4- and 1,5-substitution in the triazole ring were found in a 64:36 ratio.

Bisazides with internal triple bonds as AB_2 monomers (**19−1**) for the synthesis of hyperbranched poly(triazoles) have been independently developed by Voit et al.[242] and Smet et al.[243] As mentioned earlier, the high stereocontrol achieved by the Cu[I] catalyzed click chemistry does not apply for substituted alkynes. Thus, only a classical thermally induced

diates may permit influencing the degree of branching. Usually very high yields can be achieved; however, this high reactivity of the starting compounds can also lead to adverse side reactions between the 1,3-dipoles such as dimerizations and rearrangements (e.g., sigma tropic shifts), and therefore, the reaction conditions have to be selected carefully.

So far only two types, out of the large variety of possible 1,3-dipolar or [3 + 2]-cycloaddition reactions, have been employed for the preparation of dendritic polymers. The reaction of organic azides with alkynes forming a triazole ring has experienced an enormous revival in many fields of polymer science after Sharpless[229,230] and others[231−233] pointed out that, with suitable copper catalysis, complete control of the regioselectivity can be achieved. The term "click chemistry" has become commonplace for this hugely popular reaction due to a combination of this regioselectivity with easily accessible monomers, very high yields, and insensitivity of this reaction to many functional groups.

The other approach used so far for the preparation of dendritic structures is based on the so-called "criss-cross" cycloaddition of bisazines,[234] which always react in a two-step dual [3 + 2]-cycloaddition via an instable azomethine imine 1,3-dipole intermediate.[235]
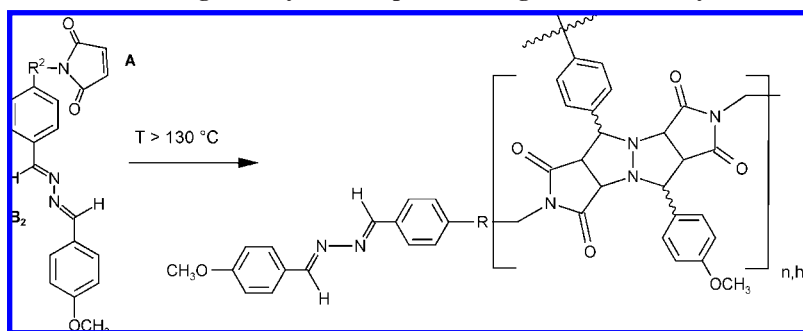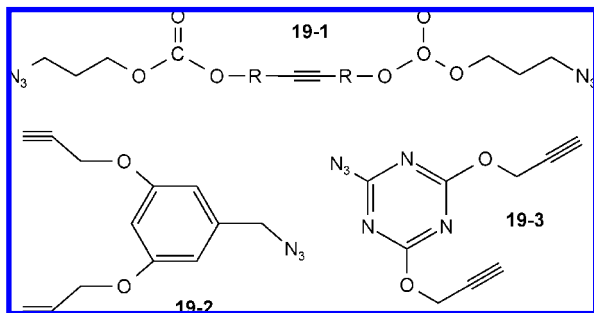
Maier, Voit et al.[236,237] used the criss-cross cycloaddition reaction to the formation of hyperbranched polymers. For that, an AB_2 monomer containing the bisazine moiety (B_2 unit) as well as a maleimide function (*A* unit) was designed and synthesized (Scheme 18). Because of the special features of this reaction and the instable azomethine imine intermediate, it was possible to achieve hyperbranched polymers

Scheme 18. *AB*₂ Monomer and the Resulting hb Polymers Prepared through Criss-Cross Cycloaddition Reaction

Scheme 19. *AB*₂ Monomers Leading to hb Polytriazoles through 1,3-Dipolar Cycloaddition

Scheme 20. *A*₂ + *B*₃ Approach Towards an Azobenzene Containing hb Polytriazole[249]

1,3-dipolar CA reaction will occur, leading again to a mixture of 1,4- and 1,5-substituted triazoles, but it was possible to achieve fully soluble products of high molar mass ($\bar{M}_n$ = 10 000 g/mol) by low temperature (45 °C) self-polymerization in bulk from the *AB*₂ bisazido monomer.[242] The resulting product bears a large number of highly reactive azide groups that present an opportunity for a large spectrum of further end group modifications. It is most suitable to use again the reaction with functional terminal alkynes or the postmodification due to the easy and highly efficient reaction. Recently, Malkov et al.[244] reported another suitable *AB*₂ monomer, 2-azido-bis(propynyloxy)-1,3,5-triazine (**19**−**3**), which was also converted successfully into a hb polymer through 1,3-dipolar cycloaddition reaction.

It is still rather difficult to produce hyperbranched polymers via the *AB*₂ approach through cycloaddition reactions due to the high reactivity of the functionalities and thus problems of monomer isolation and the danger of premature polymerization. Therefore, one can assume that 1,3-dipolar CA of alkynes with azides by the *A*₂ + *B*₃ approach has a better chance for commercial application, because suitable *A*₂ and *B*₃ monomers are readily available. In this regard, Finn et al.[245] reported on the synthesis of linear but also branched polymers prepared by di-, tri-, and tetra-alkyne and azide monomers like the combination of tripropargylamine (*B*₃) and (dihydroxymethyl) (diazidomethyl)amine (*A*₂) (compare the general outline in Scheme 17). The products that were obtained from a vast variety of multifunctional alkynes and azides formed excellent networks at high functionality conversion, had very good adhesive properties, and significantly outperformed commercial adhesives.[246,247] Acid-responsive gels, prepared from aliphatic diazides and tripropargylamine, were observed to swell and shrink rapidly in halogenated solvents depending on the acid content.[248]

Xie et al.[249] reported the synthesis of azobenzene containing hb polymers by the one-pot reaction of 4-bis(3-azidopropyl)amino-4′-nitroazabenzene with 1,3,5-tris(alkynyloxy)-benzene under typical click conditions in a 1:1 ratio of *A*₂

to *B*₃ (Scheme 20). Soluble polymers with molar masses M_w of about 15 000 g/mol were obtained and no gelation was observed, even after 48 h reaction time.

Cycloaddition reactions and especially the 1,3-dipolar CA of alkynes and azides are also very versatile in order to functionalize hb polymers through postmodification[250] or to combine linear and hb structural units. Thus, Frey et al. reported azide end-capped hb polyglycerols, which provide a versatile base for complex polymer architectures, e.g., by adding alkyne functionalized linear poly(ethylene glycol) to the azide functionalized hb core.[251]
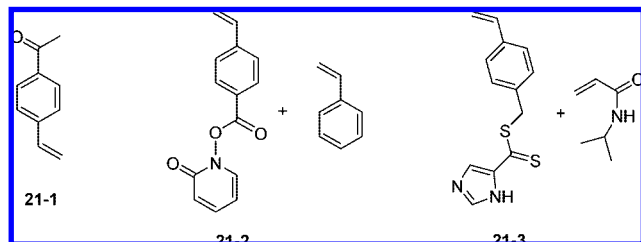
2.2.4. hb Polymers through Self-Condensing Vinyl Polymerization

As already outlined in section 2.1.2, self-condensing vinyl homo- and copolymerization is a versatile methodology to produce a variety of highly branched polymers based on a C−C chain where the degree of branching can be readily adjusted by the reactivity of the two reaction sites of the inimer and the comonomer addition.[5−7,13,32] Most of the products described are styrene or (meth)acrylate based produced by homoself-condensation or copolymerization.[121] For the styrenic inimers, various chain reactions like anionic,[252] cationic,[30,253] and various controlled radical polymerizations[110−114] have been applied. Weber and Lu[115] described the self-condensation of 4-acetystyrene (**21**−**1**, Scheme 21) by ruthenium catalysis. Polymerization occurs by Ru-catalyzed addition of C−H bonds, which are adjacent to the activating acetyl group across the C−C double bond of the vinyl group in both a Markovnikov and an anti-Markovnikov manner.

In general, copper or nickel based ATRP has been employed for the SCVP of (meth)acrylates (**3**−**5**, Scheme 3).[112,117,124,254,255] Group-transfer polymerization was used for a silylketene acetalfunctional methacrylate (**3**−**4**, Scheme 3).[108,121]

Vinylether inimers, like 1-[(2-vinyloxy)ethoxy]ethyl acetate (**3**−**3**, Scheme 3), were polymerized to give dendritic macromolecules through cationic polymerization in the

Scheme 21. Monomers and Monomer Combinations for the Preparation of Highly Branched Polymers through Chain-Growth Mechanisms: 4-Acetylstyrene Self-Condenses under Ruthenium Catalysis; Barton Ester Has Been Used in Radical Copolymerization with Styrene; The Inimer Was Copolymerized with *N*-isopropylacrylamide (NIPAM) in a RAFT Copolymerization

Scheme 22. Examples for *AB_x* and *AB** Monomers Suitable for Proton Transfer and ROMBP

presence of zinc chloride.[256] Highly branched poly(NIPAM) have been prepared using the technique of reversible addition−fragmentation chain transfer (RAFT) polymerization using a chain-transfer agent that allows the incorporation of imidazole functionality in the polymer chain-ends (**21**−**3**, Scheme 21).[114,257]

Recently, Wooley et al.[258] described the synthesis of amphiphilic hyperbranched fluoro-homopolymer and fluoro-copolymers with tri(ethylene glycol) units incorporated at the molecular level by atom transfer radical self-condensing vinyl homopolymerization of an inimer, 4-[oxy(tri(ethylene glycol))bromoisobutyryl]-2,3,5,6-tetrafluorostyrene (see **35**−**1**, Scheme 35), and copolymerization of the inimer with 2,3,4,5,6-pentafluorostyrene. The presence of tri(ethylene glycol) units in the hb fluoro-containing polymers resulted in the formation of water-dispersible micelles.
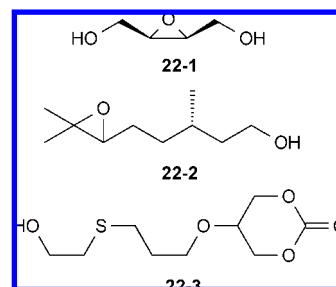
A thermally and photochemically labile styrenic Barton ester monomer of the *AB* type was the base for highly branched polystyrene copolymers as described by Cormack et al. (**21**−**2**, Scheme 21).[259] This approach is somewhat similar to that of NMRP, and highly branched, soluble products were obtained with residual Barton ester functionality that enabled their use as macroinitiators in subsequent polymerizations.

2.2.5. hb Polymers through Ring-Opening Multibranching Polymerization

As discussed previously in section 2.1.2, the ring-opening multibranching polymerization (ROMBP) or self-condensing ring-opening polymerization (SCROP) rely on the same principle of inimers, only in this case the monomer function is a heterocyclic group and a cationic or anionic mechanism is applied.[32] Polyethers[135,131,130] and polyesters[132] are mainly prepared in academia, with the hb polyglycerols[134,135] being the most prominent example that has also been commercialized by HyperPolymers.[22] By now even very high molar mass products of M_n up to 700 000 g/mol and narrow polydispersity (1.1−1.4) can be prepared from glycerol **6**−**6** using dioxane as an emulsifying agent.[260] Another well-known hyperbranched polymer produced in large scale by ROMBP is polyethyleneimine (PEI), known now under the trade name Lupasol from BASF SE, which was commercialized first under the name Polymin in 1942.[261]

Suzuki et al.[31,262] used cyclic carbamates like 5,5-dimethyl-6-ethenylperhydro-1,3-oxazin-2-one with palladium catalysis to prepare hb polyamines containing unsaturated units within the backbone (Scheme 6, **6**−**2**).

Highly branched polyesters have been prepared by macromonomers containing poly(ε-caprolactone) linear chains that had been protected at one chain-end by bis-methylolpropionic acid,[263] an approach which was similarly adopted by Frey et al.[156] for an even more simpler one-pot system using ε-caprolactone and 2,2-bis(methylol)butyric acid (Scheme 8).

Recently, hb polycarbonates have been prepared using a cyclic carbonate *AB_2* type monomer, 5-{3-[(2-hydroxyethyl)thio]propoxy}-1,3-dioxan-2-one (**22**−**3**, Scheme 22).[264] The presence of glycerol and carbonate residues in the repeating unit makes the polymer potentially biodegradable and biocompatible, promising material for drug delivery. Hyperbranched polyterpene alcohols were prepared by the cationic ring-opening polymerizations of citronellol oxide (**22**−**2**).[265] Hyperbranched carbohydrate polymers were obtained, e.g., from 2,3-anhydroerythritol using boron trifluoride diethyl etherate as a cationic initiator (**22**−**1**). The polymerizations proceeded through a ring-opening reaction with a proton-transfer reaction to produce hyperbranched polymers consisting of DL-threitol units.[266]
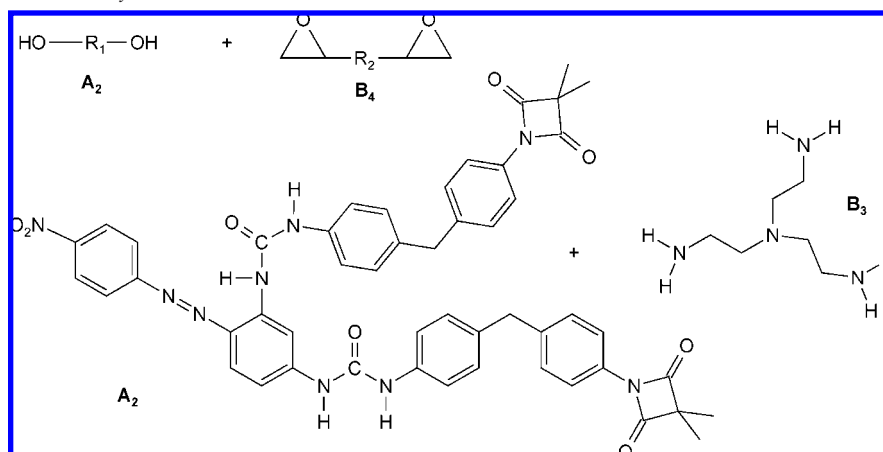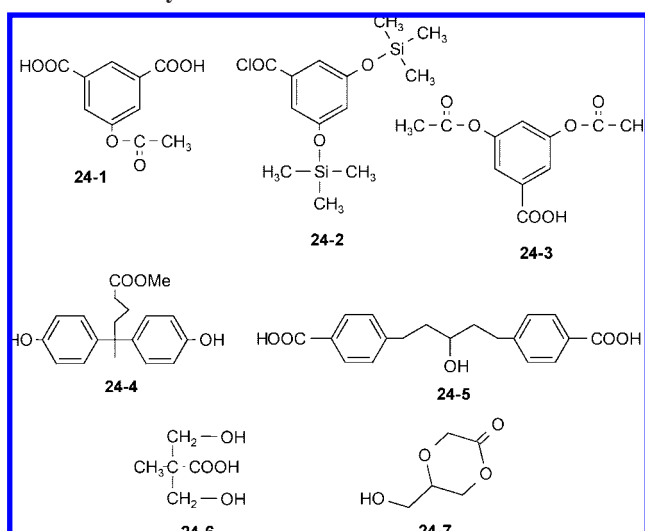
The $A_2 + B_y$ concepts have also been applied for ROMBP. Thus, Hult et al.[267] prepared polymers with linear and branched architectures through cationic ring-opening polymerization of dimethyl trimethylene carbonate using a series of polyols as initiators and fumaric acid as catalyst. The resulting materials were studied for use in powder coatings. Second-order nonlinear optical hyperbranched polymers were successfully synthesized via ring-opening addition reaction between azetidine-2,4-dione using an A_2-type monomer (Scheme 23) and primary amines in a B_3-type monomer.[268] This synthetic scheme yields products that are easily purified in short reaction times and in high yields.

Thermoresponsive highly branched polyethers were prepared via one-step proton-transfer polymerization of 1,2,7,8-diepoxyoctane (B_4) and multiols including ethylene glycol, di(ethylene glycol), tri(ethylene glycol), 1,2-propanediol, and glycerol (Scheme 23).[269]

A novel highly branched copolyether was obtained via the cationic ring-opening polymerization of 3-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}methyl-30-methyloxetane(MEMO)and3-hydroxymethyl-3′-methyloxetane(HMO) for potential use as solid polymer electrolyte.[270] In this composition, HMO was employed to create the hyperbranched structure, whereas MEMO was responsible for the ionic transportation in the resulting copolymers.

2.2.6. hb Polyesters

Polyesters are, besides the commercial hyperbranched poly(ethylene imine), a dominating class of materials in the field of hyperbranched products. The reason for that is, on

Scheme 23. Examples of $A_2 + B_y$ Monomer Combinations for Proton Transfer and ROMBP[269,268]

Scheme 24. Examples of AB_x Monomers for the Synthesis of Various hb Polyesters

the one hand, the success of the commercially available Boltorn-type aliphatic hyperbranched polyesters and, on the other hand, the relative ease of synthesis and availability of suitable monomers. In addition, polyesters have in general a high level of commercial importance, and a variety of well-known processing technologies are available. Thus, aliphatic, lower molar mass polyesters can be used very effectively in coatings and resins, and the combination of the property profile of polyesters with high functionality, low viscosity, and improved miscibility make the hyperbranched products in these fields very attractive.

Branched polyesters have been extensively reviewed recently by Long et al.,[53] with special focus on branching dilution, and have been covered thoroughly by our own work.[13] Some of the very early work is related to hyperbranched copolyesters,[26,60] and considerable research in the early 1990s addressed aliphatic,[65] aliphatic–aromatic,[15] and aromatic[61–64,66] hb polyesters, all based on AB_2 acid/alcohol monomers. For all-aromatic polyesters, prepared usually in melt-phase reaction, it was necessary to activate the phenolic groups in the monomers, as it is commonly done in polyester synthesis.[26] Acetylation of the phenolic group (**24–1**, **24–3**, Scheme 24)[63] for acidolysis polymerization and the reaction of trimethylsilyloxy groups with acid chlorides were used.[61–63] The highly activated aromatic AB_2 monomer 3,5-bis(trimethylsiloxy)benzoyl chloride (**24–2**) leads in bulk polycon-
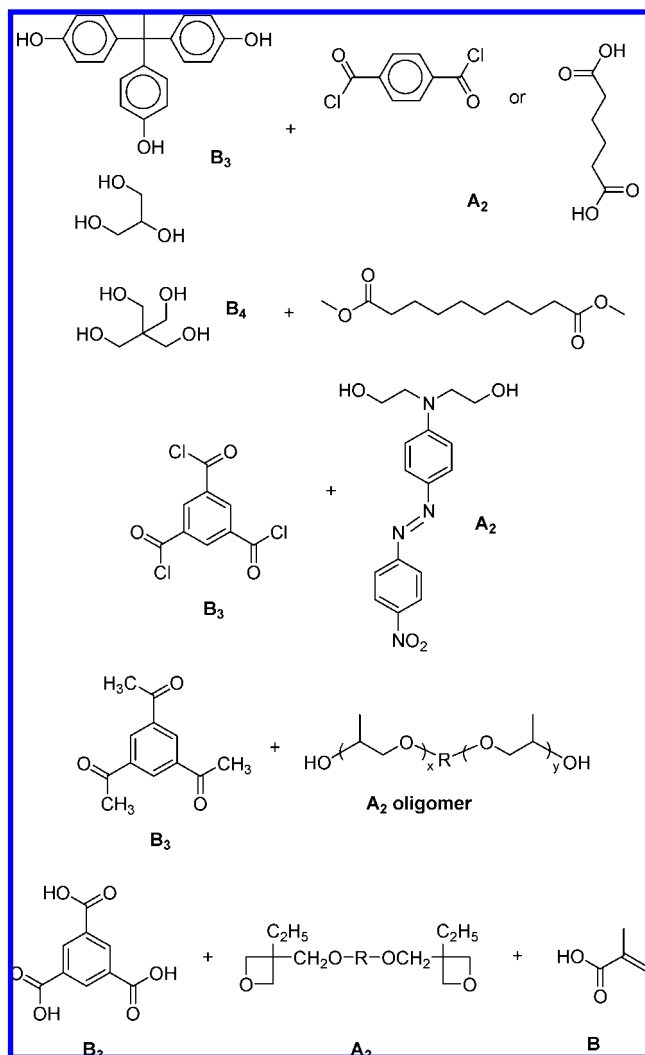
densation to a relatively high degree of branching of about 60%, since the once-reacted monomer activates the second condensation step.[271,272] Also slow monomer addition using 1,1,1-tris(hydroxymethyl)propane as B_3 core molecule in combination with **24–2** was explored by Frey et al.[273] and led to an even increased degree of branching of 64%. With a different core moiety, 1,3,5-tris(2-hydroxyethyl) cyanuric acid, was co-condensed with 3,5-dihydroxybenzoic acid in a slow monomer approach, and a degree of branching of the polyesters of 70–80% was reported.[274]

An easily available AB_2 monomer, bis(4-hydroxyphenyl)-pentanoic acid (**24–4**), can be used without any further modification directly in melt,[15,16] but also in solution poly-condensation.[275] This monomer, in which the phenolic groups are on separated aromatic units, undergoes ideal statistical AB_2 polycondensation with a very low tendency toward any side reaction or cyclizations, and a degree of branching of 50% is achieved.[15,16] Thus, this polymer was used in model studies[16] as well as intensively investigated in various application studies like in coating[276,277] and nanocomposite[278] formulations, often by modifying the end groups.[279,280] Branching could be systematically diluted by copolycon-densation with an AB monomer.[281]

The field of hb aliphatic polyesters is focused around bismethylolpropionic acid (**24–6**), the base monomer of Boltorn, and variation of that structure by applying different core moieties, adding the monomer slowly, and varying the end groups.[10] This easily available and much used monomer has as a disadvantage that cyclization[67,282] as well as side-reactions[283] can occur during polycondensation.

Similar to Fréchet's[132] use of 5-(2-hydroxyethyl)-ε-capro-lactone (**6–5**, Scheme 6) in a ring-opening polymerization, novel cyclic monomers like hydroxymethyl-1,4-dioxan-2-one (**24–7**) were used in ROMBP in the presence of Sn(Oct)$_2$ to afford the corresponding hyperbranched aliphatic poly-(ether ester).[284] This approach has been described in parallel also by Parzuchowski et al.[285]

As one could expect, also the $A_2 + B_3$ approach has been explored for the hb polyester synthesis (Scheme 25). Long et al.[286] described the solution polycondensation of bisphenol A (A_2) and 1,3,5-benzenetricarbonyl trichloride (B_3) in solution at 25 °C to prepare hyperbranched poly(aryl ester)s. Gelation was avoided by adding the bisphenol slowly to a dilute solution of the acid chloride and using a molar ratio A_2/B_3 of 1:1. A degree of branching of about 50% was reached under those conditions. This approach was adopted by us in a kinetic study on $A_2 + B_3$ aromatic and aliphatic

Scheme 25. Examples of $A_2 + B_y$ (+B) Monomer Combinations for the Preparation of hb Polyesters

polyester synthesis using the reaction of the aromatic terephthaloyl chloride (A_2) and the aliphatic adipic acid (A_2), respectively, with 1,1,1-tris(4-trimethylsiloxyphenyl)ethane (B_3) and 1,1,1-tris(4-hydroxyphenyl)ethane (B_3).[287] The experimental results on the development of the structural units matched theoretical predictions.[288] Adipic acid has been also used by Stumbé and Bruchmann[20] in combination with glycerol (B_3) (Scheme 25) to prepare commercially interesting hb aliphatic polyesters with high molar mass and without gelation by controlling the reaction time, viscosity, and initial molar ratio of adipic acid and glycerol. Pentaerythritol was polycondensed with dimethyl sebacate 1.2/1.0, in bulk at 240 °C by Kricheldorf and Behnken,[289] resulting in a soluble viscous resin that is biodegradable (Scheme 25).

Other aliphatic $A_2 + B_3$ systems have been described by Fossum et al.[290] who used glycerol or trimethylolpropane as B_3 monomers and fumaric acid as A_2 monomer, which led to an unsaturated hb polyester. Hyperbranched polyesters with many pendant hydroxyl groups that were in situ modified with acrylate functions were prepared by polyaddition of bisoxetanes to 1,3,5-benzene tricarboxylic acid in NMP solution followed by addition of monofunctional methacrylic acid (Scheme 25).[291] Similarly, hyperbranched polyesters with terminal methacryloyl groups and medium molar mass were synthesized by the one-pot polyaddition of bisphenol A diglycidyl ether and trimesic acid in the

presence of methacrylic acid in good yields.[292] The addition of a monofunctional B molecule to an $A_2 + B_3$ approach allows control of gelation.[53,293]
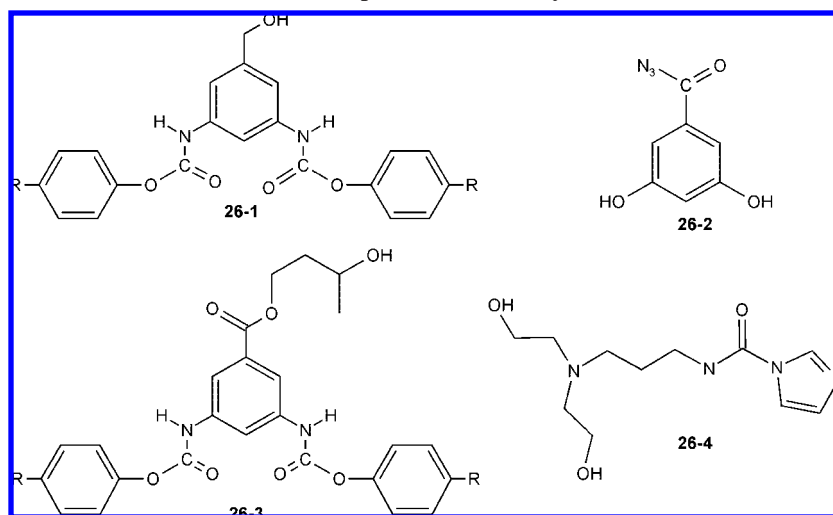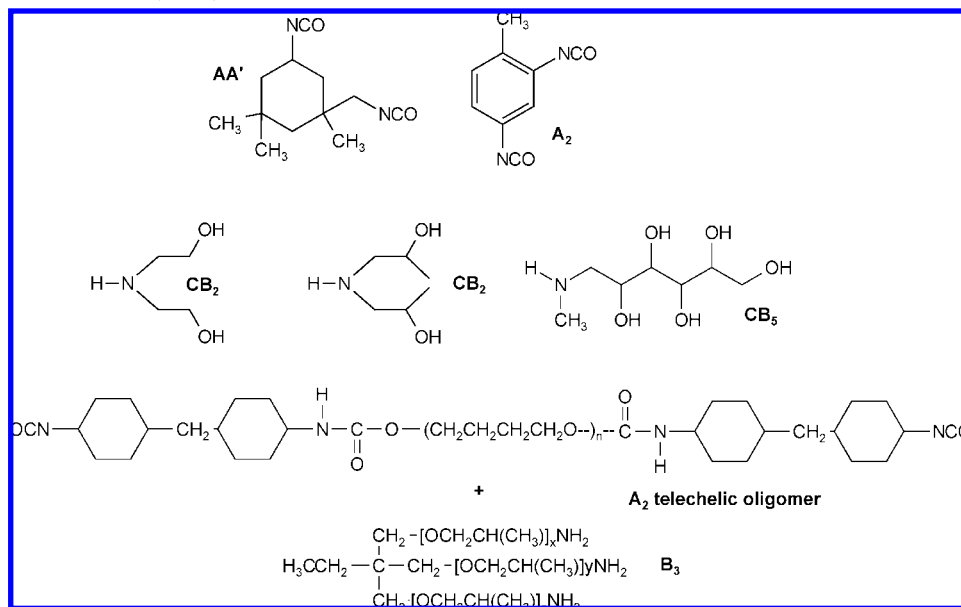
The various concepts to introduce some branching into polyesters and how the branching influences the material properties in solution, melt, and bulk have been summarized by Long et al.[53] The methodologies cover the classical addition of a B_y monomer to A_2 and B_2 monomers with and without a monofunctional end-capping agent as well as the copolycondensation of AB with AB_2 monomers. One example for that is also given by Frey et al.,[156] who combined the AB_2 polycondensation with ROP of ε-caprolactone (Scheme 8). This reaction could also be carried out under enzymatic catalysis using immobilized Lipase B under mild conditions.[294] A simple highly versatile enzymatic route to prepare hyperbranched aliphatic polyesters with dendritic trimethylolpropane units was also described by Gross using a $A_2 + B_2 + B_3$ approach.[295,296] By using lipase-catalysis instead of alternative chemical approaches, highly functional branched copolymers of substantial molecular weight were formed with no gel content, and through systematically varying the trimethylolpropane content in the copolymers, products with DB values ranging from 15 to 67% were obtained.

Oligomeric A_2 monomers like poly(propylene glycol) can be combined with B_3 moieties (trimethyl 1,3,5-benzenetricarboxylate) as described by Unal and Long[297] for the synthesis of highly branched poly(ether esters) in a cyclization-free melt condensation (Scheme 25). To avoid gelation, the reaction had to be stopped before reaching the theoretical critical conversion, which agreed with the experimental gel points, indicating low amounts of intramolecular cyclizations. Monofunctional end-capping reagents were also used to avoid gelation in the melt phase, and high molar mass final products were obtained with nearly quantitative monomer conversion in the absence of gelation. Further details on the characterization of branched polyesters will be provided in section 3.

2.2.7. hb Polyurea and Polyurethanes

Branched materials containing urea or urethane groups within the backbone are well-known as precursors toward various polyurethane (PU) resins and foams, and thus, they have high industrial importance. In general, isocyanate chemistry is well-explored for polymer materials due to the high versatility and the potential to fine-tune material properties by the structure of the monomers, various monomer combinations, and morphology and branch point density control. Hydrogen bonding plays an important role in this class of materials, and these noncovalent interactions often significantly determine the material properties.[298]

Dendritic structures are also known in the field of polyurethanes but, due to the high reactivity of the isocyanate groups toward the hydroxyl groups and the tendency toward side reaction, it is a challenging task to prepare well-defined branched architectures and, especially, to isolate suitable AB_2 monomers. Bruchmann[19] recently summarized comprehensively the synthesis and applications of dendritic polyurethanes. The first two hyperbranched PUs were reported in 1993. Spindler and Fréchet published the phenol blocked 3,5-diisocyanatehydroxybenzyl (**26−1**, Scheme 26) as AB_2 monomer,[191] and Kumar and Ramakrishnan reported the Curtius rearrangement of azides as an isocyanate-free process (**26−2**),[192] which was later expanded toward hb polymers bearing oligoethyleneoxy spacer segments.[299]
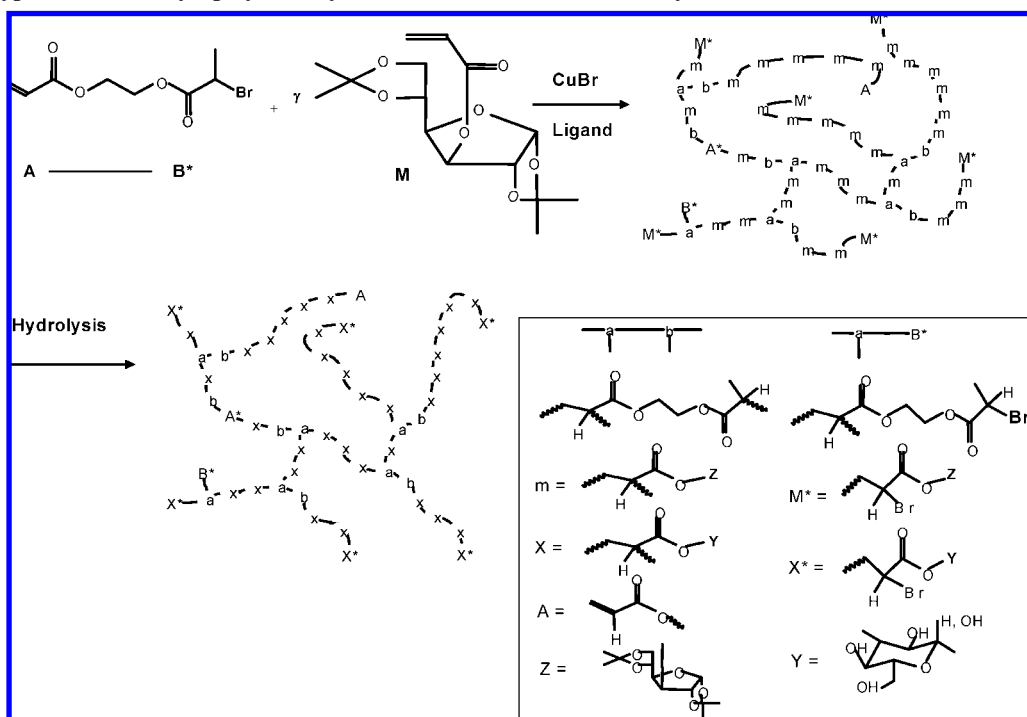
Scheme 26. Examples of AB_2 Monomers Used for the Preparation of hb Polyurethanes

Scheme 27. Examples of $A_2 + B_y$ (CB_{y-1}) Monomer Combinations for the Preparation of hb Poly(urea urethane)s

In the first approach, the reaction was started by the thermal deblocking of the isocyanate groups, and PU of up to 34 000 g/mol (M_w) could be isolated. Nasar et al. expanded that approach toward hb PU exhibiting ether or ester linkages as chain-extending units by employing corresponding AB_2 monomers (**26**–**3**).[300] Higher molar mass products with better solubility and higher thermal stability resulted. Also Bruchmann et al.[301] prepared blocked AB_2 monomers by employing readily available monomers, like 2,4-toluylene diisocyanate, hexamethylene diisocyanate, trimethylolpropane, or diethanolamine. For this chemistry, the diisocyanate was reacted 1:1 with, e.g., trimethylolpropane, which was monofunctionalized by ketalization with acetone followed by a second addition of butanone oxime at the remaining NCO group. After cleavage of the ketal and thermal activation of the oxime blocked NCO group, the resulting AB_2 intermediate reacted to hb polyurethane polyols.

The Curtius rearrangement approach by Kumar and Ramakrishnan[299] was also followed by Tang and co-workers,[302,303] generating oliogoethyleneoxy modified dendritic polyurethanes with improved ionic conductivity in combination with linear polyurethanes and lithium perchlorate compared to a pure linear setup.

An isocyanate free approach was reported by Rannard et al.[304] based on the selective reaction between carbonyl diimidazole and N-(3-aminopropyl) diethanolamine, forming a urea intermediate (**26**–**4**) as active AB_2 species. Again, polyaddition was induced thermally.

Since the AB_x approach requires rather innovative chemistry approaches due to the high reactivity of the NCO group, researchers quickly adopted the $A_2 + B_y$ approach for hb polyureas and polyurethanes to simplify the process and to work with more easily available monomers. Thus, hyperbranched PU polyols and polyisocyanates could be prepared based on conventional PU raw materials, making use of differences in reactivity in an $A_2 + CB_2$ or $AA' + CB_2$ (or $AA' + B'B_2$) approach.[96,97,305] For example, 2,4-toluylene diisocyanate (A_2) or isophorone diisocyanate (AA') is reacted with diethanolamine or diisopropanolamine (CB_2), forming polyurea urethanes (Scheme 27). The reaction is carried out in a two-step method. At low temperature preferentially, the amino functions react first with one isocyanate group, leading to an urea containing AB_2 intermediate. By increasing the temperature to room temperature and above, polyaddition to the urethane units takes place. The reaction is stopped by adding a monofunctional end-capper or excess of the

Scheme 28. Hyperbranched Glycopolymers by SCVCP of an Inimer with a Glycomonomer[315]

dialcoholamine, and via real-time attenuated total reflection−infrared (ATR-IR) spectroscopy, the progress of the polyaddition could be directly followed and controlled.[306] The complex structure of the hb products could be elucidated via NMR spectroscopy,[98] verifying a degree of branching of 45−71% depending on the monomers used. Structural effects and end group effects of these hb poly(urea urethane)s in bulk and in thin films have been further investigated, and it was shown that, due to strong hydrogen bonding in the backbone, the effect of the nature of the end groups is less dominant than it is, e.g., in polyester structures.[307] HB poly(urea urethane) could also be prepared by $A_2 + CB_5$ monomer combination (Scheme 27)[97] by using various diisocyanates in combination with 2,3,4,5,6-pentahydroxy-N-methylhexylamine. Branching could be verified, even though the reactivity of the primary alcohol was higher than that of the secondary ones.

An oligomeric $A_2 + B_3$ approach toward hyperbranched segmented poly(urethane urea) elastomers was reported by Long et al.[308] based on linear isocyanate terminated urethane prepolymers prepared by reacting difunctional poly(tetramethylene oxide) or poly(propylene oxide) oligomers with bis(4-isocyanatocyclohexyl)methane (HMDI). These A_2 units were added slowly to a solution of low molar mass or oligomeric triamines (Scheme 27). Gelation in this system was somewhat shifted to higher conversion values than theoretically expected due to a high tendency for internal cyclization. The resulting products showed microphase-separated morphologies and mechanical properties close to their linear analogues.[309] It could be proven that branching was successfully implemented in the structures with a degree of branching of 30−50%, and thus, rheology investigations showed, as expected, a strong decrease in melt viscosity for those long-chain branched products in comparison to a linear polymer.[310]

Additionally, hyperbranched PU architectures were achieved by employing hb polyetherols or polyesterols or hb poly(urea

urethane)s with alcohol or isocyanate end groups in PU coating formulations.[19,311] This is a fast-expanding field.
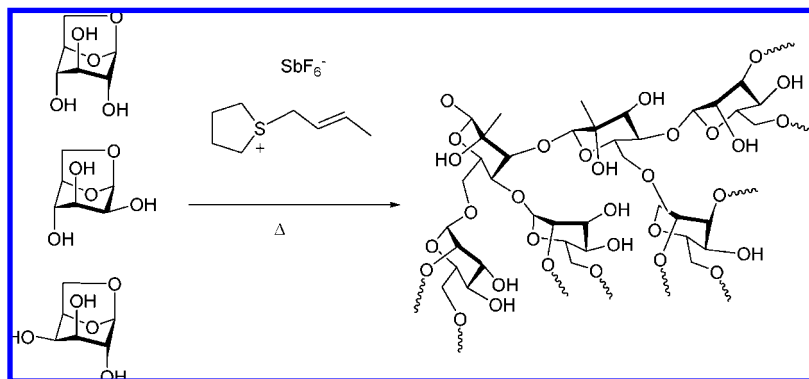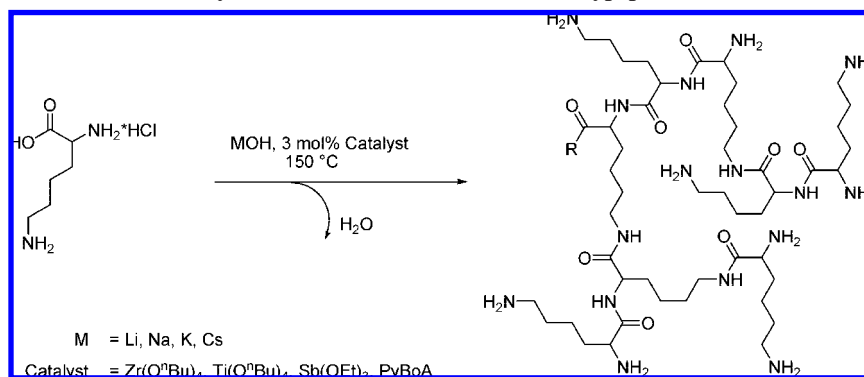
2.2.8. Hyperbranched Glycopolymers and Polypeptides

Over the past several years, interest has increased in the use of hb polymers in various biomedical applications that require specific biocompatibility of the respective materials. hb polyglycerols, hb products containing poly- or olio(ethylene glycol) units, and biodegradable materials like aliphatic polyesters are promising candidates for that application. Biocompatibility can be further combined with biofunctions; therefore, sugar units or peptidic linkages have been incorporated into the highly branched structure, as it has been well-explored already for dendrimers.

One possibility is to introduce suitable end groups into a preformed hb polymer. This concept was recently used to introduce, through basic amidation chemistry, maltose and maltotriose units into hb poly(ethylene imine)s, creating a dense carbohydrate shell which that the products highly biocompatible.[312] Hyperbranched poly(amido amine)s containing tertiary amines in the backbones and acryl terminal groups were prepared via the Michael addition polymerization of trifunctional amines with a 2-fold molar excess of diacrylamide. The hb polymers were further modified with glucosamines though end group modification.[313]

Glyco-units can also be incorporated into the repeating units by SCVP or ROMBP. Müller et al.[314] copolymerized the methacrylic AB* inimer 2-(2-bromoisobutyryloxy)ethyl methacrylate with 3-O-methacryloyl-1,2:5,6-di-O-isopropylidene-R-D-glucofuranose (MAIGlc) via ATRP using the $(PPh_3)_2NiBr_2$ catalyst system in solution. Deprotection of the isopropylidene protecting groups of the branched poly-(MAIGlc)s resulted in water-soluble glycopolymers with randomly branched architectures, which showed high biocompatibility and supported cell growth.[315] Satoh and Kakuchi[316] recently summarized the use of anhydro sugars as inimers for the preparation of hb carbo-

Scheme 29. Hyperbranched Carbohydrate Polymers from 1,6-Anhydro-b-D-gluco(manno, galacto)pyranose through Cationic ROMBP[321]

Scheme 30. Direct Self-condensation of L-lysine as AB_2 Monomer to an hb Polypeptide[332]

hydrate polymers via ROMBP, which leads to sugar units directly within the backbone (Scheme 28). For example, Schuerch et al.[317] and others[318] reported the synthesis of highly branched polysaccharides prepared from 1,6-anhydro-b-D-hexopyranose using monochloroacetic acid for initiation of the cationic polymerization. This solid-phase polymerization, however, has the disadvantage of a heterogeneous initiation reaction, which led to a broad polydispersity. This problem could be overcome by solution polymerization of 1,6-anhydro-b-D-hexopyranose using a thermally induced cationic initiator.[319] The carbohydrate monomer can be considered as an AB_4 moiety. Similarly, other anhydro sugars were explored like 1,4-anhydroerythritol and 1,4-anhydro-L-threitol using trifluoromethanesulfonic acid or fluorosulfonic acid[320] as initiators, as well as 2,3-anhydroerythritol and 2,3-anhydro-DL-threitol, which can be considered as AB_2 monomers.[266] Other structures cover, e.g., hyperbranched poly(2,5-anhydro-D-glucitol) by proton-transfer cyclopolymerization of 1,2:5,6-dianhydro-D-mannitol (Scheme 29).[321]

On the other hand, Kadokawa et al.[322] reported the synthesis of a hyperbranched polyaminosaccharide by the acid-catalyzed polymerization of an oxazoline sugar having two hydroxyl groups as an AB_2-type monomer.

Various complex branched polypeptide architectures applying N-carboxyanhydride (NCA) polymerization were summarized by Kricheldorf[323] and Klok.[324] Dendritic polypeptides were first created in a stepwise manner using N-protected L-lysine-NCAs.[325,326] Hyperbranched polylysine graftcopolymers (dendrigrafts) were recently obtained by a combination of ROP of N'-Z-L-Lys-NCA or N'-TFA-L-Lys.-NCA with a stepwise introduction of branching points through N''-,N'-bis-Fmoc-L-lysine.[327] The Fmoc groups were selectively removed by means of pyridine so that N'−Z and N'−trifluoroacetyl (TFA) groups of the linear segments

remained unchanged. Alternatively, N'-Boc or N'-TFA-L-Lys-NCA was grafted on linear poly(L-lysine) with free amino groups. The ε-amino groups of the new side chain were deprotected and the free amino groups served again as initiators for the N'-protected L-Lys-NCA.[328] But also various graft copolymers, branched-linear hybrids, and star-type structures were created.[323,324]

Hyperbranched polypeptides through amino acid AB_2 monomers are still rare. One example has been reported by Menz and Chapman,[329] who explored the synthesis of hyperbranched polylysine using the N-hydroxysuccinimide ester of L-lysine dihydrochloride as AB_2 building block. Slow monomer addition to a tri- or hexafunctional core yielded hyperbranched polylysines with $M_n = 12\,000{-}16\,000$ g/mol. Hyperbranched poly(L-lysine)s were also prepared by Vlasov et al.[330] through catalytic removal of a N-ε-carbobenzyloxy blocking group from N-ε-carbobenzyloxy-L-lysine-N-carboxyanhydride by hydrogenation in the presence of an activated palladium. Under similar conditions, hb poly(amino acids) containing residues of glutamic acid or alanine were prepared.

The simple thermal self-condensation of L-lysine hydrochloride can be applied for the synthesis of hyperbranched polylysines as reported in detail recently (Scheme 30).[331,332] Because of the unequal reactivity of the two amine groups of L-lysine hydrochloride, thermal polymerization of this asymmetric AB_2 monomer results in hyperbranched polymers, which contain approximately 2.5 times more N-ε-linked linear compared to N-α-linked linear structural units. The polymer architecture during the thermal hyperbranched polymerization of L-lysine hydrochloride could be controlled by modulating the reactivity of the more reactive ε-NH$_2$ group by introducing temporary protective groups that preferentially block the ε-NH$_2$ position. This was achieved

by (i) addition of *o*-vanillin to the polymerization, (ii) copolymerization of *N*-ε-benzylidene-L-lysine, and (iii) copolymerization of α-amino-ε-caprolactame.

Interestingly, the first examples of hyperbranched polypeptides date back to the 1950s and 1960s, where a number of authors investigated the thermal polymerization of amino acids, including AB_2 type monomers, such as L-aspartic acid, L-glutamic acid, and L-lysine.[333−335] However, although Flory had already theoretically described the synthesis of highly branched polymer molecules, the concept of dendritic and hyperbranched polymers was poorly developed at that time.

2.2.9. Functional Materials with hb Architectures

Hyperbranched polymers are under consideration for a variety of applications, with the coating, resin nanocomposite, and additive areas being the most prominent.[21] Also applications in biomedical areas like drug delivery, catalysis, imprinting, sensors, or various high-tech areas are proposed since the highly branched structure and the high number of end groups allows introduction of multifunctionality and fine-tuning of specific interactions.[4−6,13]
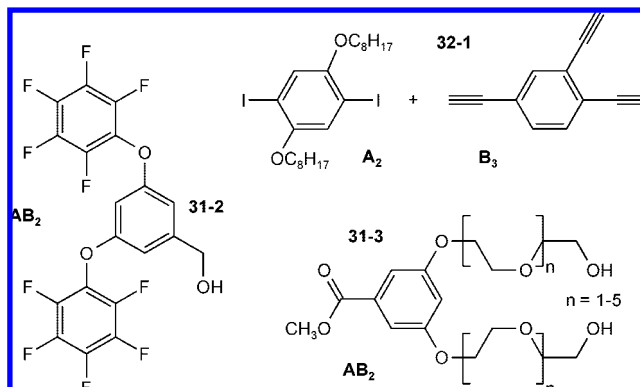
Details on the vast area of applications of hyperbranched polymers cannot be discussed here, but a few examples will be given, where specific functional hyperbranched polymers are synthesized having inherent specific optical, photonic, catalytic, magnetic, or electronic properties.

Gao and Yan[5] recently reviewed the various application areas. Special focus was placed on conjugated functional hyperbranched materials with optical, electronic, and magnetic properties that also have been the main focus of a recent review on hyperbranched macromolecules constructed from acetylenic triple bonds.[223] Clearly, the phenyl based materials prepared by the [2 + 2 + 2]-cycloaddition of various acetylenic monomers as described above (section 2.2.3)[225−228] offer a great potential for the preparation of conjugated soluble materials with special optical or electronic properties, which can be easily processed into thin films and can be patterned for applications in microelectronic or microsystem devices. Strong light emission, stable optical nonlinearity, and high photorefractivity are reported. The polymers can generate fluorescent images and can form well-aligned nanotubes. Also, the polyynes can be postfunctionalized through metal complexation, where refractive indices can be manipulated by photoirradiation. The hb polymer complexes can serve as precursors to soft ferromagnetic ceramics and as catalysts for carbon nanotube fabrication.[223] Similarly, Müllen et al.[219,336] reported the preparation of carbon nanotubes from Diels−Alder CA hb polyphenylenes and extended graphene-like sheets. On the other hand, nonconjugated hb polyphenylenes are also highly interesting as thermally stable materials with very low dielectric constants (∼2.0) suitable as insulating interlayers (dielectrica) in microelectronic devices.[217]

Hyperbranched poly(*p*-phenylene ethynylene)s (PPEs) have been reported by Weder et al.[337] through the Pd/Cu-catalyzed cross-coupling reaction of $A_2 + B_3$ monomers (**31−1**, Scheme 31). The resulting materials were highly soluble and showed the characteristic optical properties of highly conjugated PPEs.

Ionic conductivity is highly interesting in hb polymers containing ethylene glycol units. This allows their use as solid electrolytes. Hawker and co-workers[338] and also Itoh et al.[339] first prepared hyperbranched poly(ether ester)s containing linear PEG units through oligoethylene glycol

Scheme 31. Examples for Monomers to Prepare Functional hb Polymers: AB_2 Fluoro-Containing Monomers for the Preparation of Thermally Stable Hydrophobic hb Polymers; $A_2 + B_3$ Monomers for Conjugated hb Poly(phenylene ethynylene); AB_2 Monomer for Oxyethylene Containing hb Polymers with High Ion Conductivity

containing AB_2 monomers for use as ion-conducting material (**31−3**, Scheme 31). The influences of the terminal groups, the length of the PEG unit, the composition of the linear polymeric electrolytes blended, and the addition of fillers on the properties of the hyperbranched polymeric electrolytes were systematically investigated by Itoh and co-workers[340] Tang et al.[302] synthesized hyperbranched polyurethanes with EG units by polycondensation of AB_2 monomers 3,5-bis(2′-hydroxyethyleneoxy)benzoyl azide and 3,5-bis[(5′-hydroxy-3′-oxopentyl)oxy]benzoyl azide, and prepared composite polymer electrolytes using hyperbranched polyurethanes, linear polyurethanes, and LiClO4 as raw materials. Also ROMBP of oxetanes was used to prepare materials suitable for solid electrolytes.[270]

Another interesting class of hb polymers is that of fluoro containing polymers due to their special chemical stability, high hydrophobicity, potential to fine-tune surface properties, and specific aggregation and solubilizing properties, e.g., as components in micelles. Wooley et al.[341] recently summarized the synthetic approaches and properties of various hb fluoromaterials prepared by the self-polycondensation or SCVP. The incorporation of fluoro groups was a result of either the chemistry employed during polymer buildup[342−344] or a postpolymerization modification effort.[280,345] hb fluoropolymers have been studied for optical waveguide applications,[346] as additives for coatings,[280] in corrosion inhibiting coatings,[347] and as membranes for gas separation.[348] Wooley prepared fluoropolymers through fluorinated AB_x monomers like 3,5-bis[(pentafluorbenzyl)oxy]benzylalcohol (**31−2**, Scheme 31).[349] Self-condensing vinyl copolymerization (SCVCP) of fluorinated monomers like 2,3,4,5,6-pentafluorostyrene with an inimer like *p*-chloromethylstyrene[113] or by homopolymerization of fluorinated amphiphilic inimers[258] are reported. The latter aggregate to micelles with strong amphiphilic behavior. Amphiphilic cross-linked networks with hybridization of these hydrophobic hb fluoropolymers and linear hydrophilic poly(ethylene glycol)s are also discussed. As microphase-segregated materials with nanoscale surface heterogeneities, these networks possessed unusual antibiofouling abilities, atypical sequestration and release behaviors for guest molecules, and special mechanical properties.[341]

Polydimethylsiloxane (PDMS)-grafted fluorocopolymers with various branching features were synthesized based on ATRP techniques via a "grafting-through" approach using

methacryloxypropyl-terminated PDMS (PDMSMA) as macromonomer.[350] Copolymers with a linear fluorinated backbone and linear PDMS grafts were prepared by copolymerizations of 2,3,4,5,6-pentafluorostyrene (PFS) with PDMSMA. Copolymers with a hyperbranched fluorinated backbone and linear PDMS-based grafts were prepared by SCVCP of an inimer, p-chloromethylstyrene, with PFS and PDMSMA. Copolymers with a hyperbranched fluorinated core and linear PDMS grafts were prepared by ATRP of PDMSMA, initiated by benzylic chloride-functionalized hyperbranched fluorocopolymers.

As further examples, other functional hyperbranched materials are liquid crystalline (see as early example for a suitable AB_2 monomer for LC polyethers Scheme 11, **11**−**5**[68,164])[351] and allow holographic recording,[352] have photoactivity[353] or second-order nonlinear optical properties (Scheme 25),[354] exhibit photoluminescence,[355] can be used as photoinitiators,[356] and exhibit shape-memory behavior, e.g., in polyurethane based hb polyesters.[357]

2.3. Architectures with Diluted Branching and Linear-Hyperbranched Hybrids

One drawback of "classical" hyperbranched polymers with branching sites in each repeating unit is the high branching density that prevents the formation of entanglements in the bulk material, and therefore, structural applications of plain hb polymers are not possible due to high brittleness and poor mechanical properties. In addition, the structural variety is limited since, in the one-pot AB_x approach, only one polymerization type can be employed. Therefore, early in the development of hb polymers, the reduction of the degree of branching and the branching density has been explored by various approaches, which led to a broad variety of linear-hyperbranched hybrids. Comprehensive reviews in this field have been given by us,[7] and more recently by Gauthier[358] as well as by Taton and Gnanou.[105]

2.3.1. Copolymers

Branching can be diluted easily by mixing AB_x monomers with AB monomers as it has been done in a few cases for the AB_x approach,[26,53,281,359−361] and which is rather standard in the area of SCVP leading to the broad field of self-condensing vinyl copolymerization (SCVCP).[32] As already outlined, Long et al.[53] discussed in detail how the long-chain branching induced into linear polyesters by adding branching units influences the material properties. When the linear chains between the chains are long enough, the good mechanical properties of linear polymers can be combined with enhanced solubility, lowered solution viscosity, and enhanced processing possibilities.

In SCVCP, mixing of inimers with various monomers is the common procedure to prepare highly branched functional polymers like fluoropolymers, thermoresponsive materials,[114,257] glycopolymers,[314] and others. In ROMBP, especially, ROP of ε-caprolactone with AB_2 monomers has been explored.[156] Again, those methods permit combination of the positive properties of the linear polymers with improved melt and solution processing of hb polymers. In addition, very high molar mass branched products can be prepared that can be considered as nanoglobules.

Branching is also diluted by increasing the distance between the branching points using oligomeric or polymeric branched starting material of AB_x[263,362] as well as in the A_2

+ B_y approach[297,308] or by just using AB_x monomers of different molar masses and size.[363−365] This approach can also be considered a special case of arborescent polymers, which is classified as a macromonomer approach and which will be addressed below.

2.3.2. Dendrigraft and Arborescent Graft Polymers, Hyper-Macs
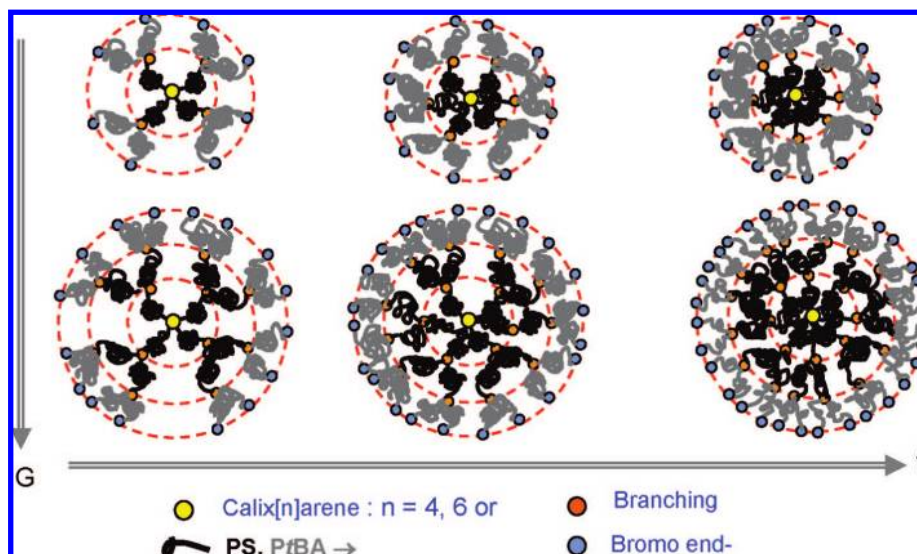
Besides the regular dendrimers and hyperbranched polymers, a new class of dendritic polymers has emerged whose branching points are linked to each other by true polymeric chains. Different names appear in the literature describing those structures like com-burst polymers,[38] arborescent graft polymers,[39,366−368] dendrigrafts,[39] polymers with dendritic branching,[140,369] and hyper-Macs.[370] These materials are generally obtained by combination of controlled polymerization techniques with selective branching reactions. A rapid increase in molar mass and in size is characteristic of the formation of the successive generations of these highly branched polymers.

The various methods described differ in the synthetic approaches as well as in the achieved control over the structure. An example of one method to prepare *dendrimer-like polymers* with very high structural control is summarized by Gnanou and co-workers[105] and uses a universal iterative strategy based on the divergent synthesis as described by Percec et al.[371] In this work, dendritic macromolecules were prepared from conventional monomers by a combination of living radical polymerization and irreversible terminator multifunctional initiator (TERMINI).[372] TERMINI is a masked multifunctional initiator that quantitatively interrupts a living polymerization. After demasking, the TERMINI-derived repeat unit provides access to a quantitative reinitiation of the same living polymerization in more than one direction, thus becoming a branching point, e.g., a combination of self-regulated metal-catalyzed living radical polymerization initiated from arenesulfonyl chlorides and the irreversible TERMINI diethylthiocarbamic acid *S*-{3-[1-(*t*-butyl-dimethylsilanyloxy)vinyl]-5-diethylcarbamoylsulfanylphenyl} ester was used to prepare dendrimer-like poly-(methyl methacrylate) (PMMA).[373]
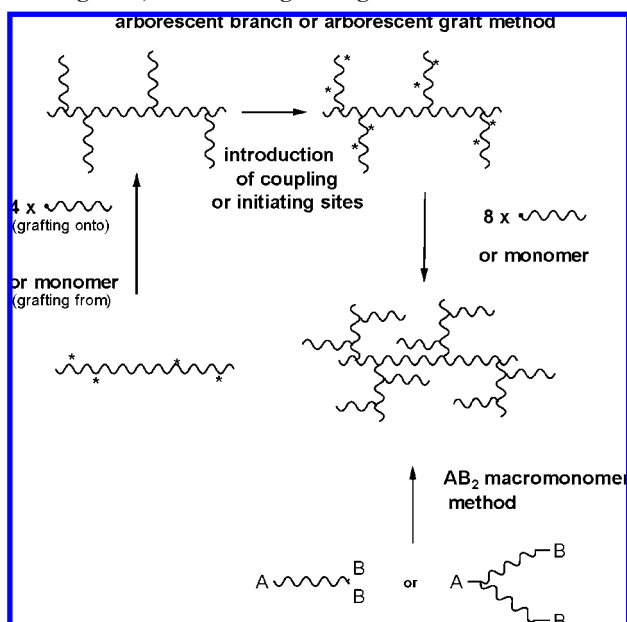
Highly branched poly(ethylene glycol)s,[374] polystyrenes,[375] poly(ε-caprolactone)s,[263] and poly(methyl methacrylate)s[104] were prepared by this process. ATRP of vinylic monomers and anionic ring-opening polymerization of ethylene oxide are two controlled polymerization techniques intensively used for this divergent approach. Scheme 32 generally outlines the approach for the ATRP synthesis of PS-P*t*BA block-copolymers. In a specific example, bromo end groups of polystyrene (PS) derived from ATRP were reacted with the amino function of diethanol amine and, subsequently, the alcohol groups underwent esterification with bromoisobutyryl bromide, allowing for two initiating sites for ATRP at the chain ends. In another example, hydroxyl-end-functionalized poly(ethylene oxide) or polystyrene had been modified with a branching agent, 2,2,-dimethyl-5-hydroxymethyl-1,3-dioxane, having two hydroxyl groups protected by the ketal ring.[374]

Gauthier and Yuan,[376] on the other hand, reported a one-pot "grafting-from" (Scheme 33) anionic copolymerization of, e.g., styrene and 1,3-diisopropenylbenzene with activation of the pendent isopropenyl moieties with *s*-butyllithium. Arborescent polystyrene-*g*-poly(*t*-butyl methacrylate) copolymers were thus obtained by addition of *t*-butyl meth-

Scheme 32. General Outline of the Synthesis of Dendrimer-Like Polymers through the Divergent Approach Showing the Growth Depending on the Core Functionality and the Number of Generations; As Example, the ATRP Synthesis of PS-P*t*BA Block-Copolymers Introducing Suitable Branching "Termini" Like Diethanol Amine at Each Generation Is Given (Scheme Provided by Gnanou and Taton; Reprinted with Permission from Ref 105; Copyright 2007 Royal Society of Chemistry)

Scheme 33. Schematic Representation of the Synthesis of Arborescent Graft Copolymers through Grafting from, Grafting onto, and Grafting through *AB₂* Macromonomers
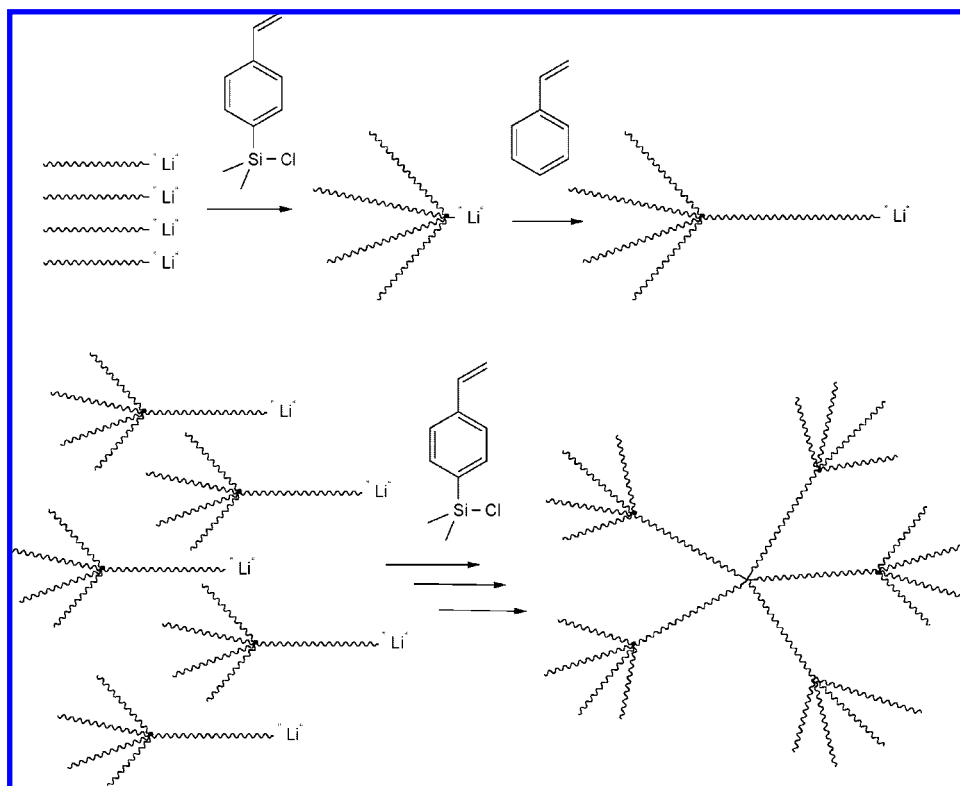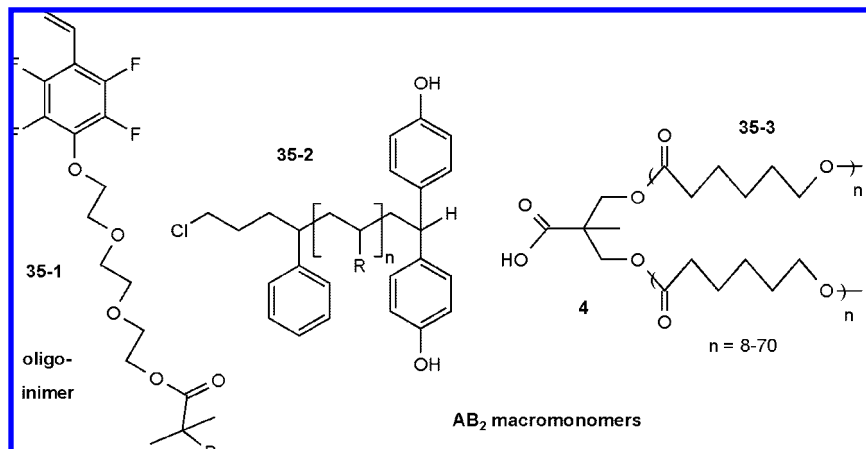

acrylate to linear and G0 macroinitiators. A multiple grafting-from technique was used also by Dworak and co-workers to synthesize arborescent-branched high molar mass poly(2,3-epoxypropan-1-ol).[377] In the first step, linear polyglycidol was obtained. Some of the hydroxyl groups were transformed into alcoholate anions in a reaction with potassium *t*-butoxide, and the obtained polyanion was used to initiate the polymerization of 1-ethoxyethyl glycidyl ether, the glycidol having a protected hydroxyl group. Removing the protecting groups yielded polyglycidol-graft-polyglycidol, and larger macromolecules were obtained by repeating the process steps. In this approach, even though high control over the chain growth is obtained, the distance between the branching points is not controlled since the initiating sites are randomly distributed along the grafted chains, and thus,

a random branching occurs more like in hyperbranched polymer than in dendrimers.

The convergent strategy toward arborescent-graft or dendri-graft polymers involving controlled polymerization techniques and grafting-onto strategies (Scheme 33) was recently reviewed by Gauthier.[40,358] The comb-burst polymers reported by Tomalia,[38] which are based on the 2-ethyl-2-oxazoline and cationic polymerization, also fall under this strategy. In contrast, Gauthier[358] relied on anionic polymerization, e.g., by grafting living PS chains onto chloromethylated PS chains. Also isoprene homopolymers with a dendritic architecture were prepared through anionic polymerization. A linear polyisoprene substrate with a high1,4-content was first epoxidized to introduce grafting sites randomly along the chain. Coupling of the epoxidized polyisoprene with poly-isoprenyllithium yielded a comb-branched or generation G0 arborescent polyisoprene. Further epoxidation and grafting of the G0 polyisoprene led to arborescent isoprene homopolymers of generations G1 and G2.[378] The distinguishing features of arborescent-graft polymers are their assembly from polymeric building blocks of uniform size and their very high molar masses obtained in a few synthetic steps.

Hirao et al.[104,379] reported on various highly branched structures based on an iterative approach using functionalized 1,1-diphenylethylene derivatives in conjunction with living anionic polymers. This strategy utilizes mixed methodologies based on both divergent and convergent approaches, since preformed well-defined polymer chains of controlled chain length are used. Thus, living PS chains are added to diphenylethylene bisfunctionalized with 1,1-bis(3-*tert*-bu-tyldimethylsiloxymethyl) groups. These functional groups are converted to benzylbromide groups, and living PS chains functionalized with diphenylethylene derivatives are grafted on those, and so on.

Knauss and co-workers[140,369] reported on a convergent synthetic approach toward dendrimer-like polymers involving 4-(chlorodimethylsilyl)styrene (CDMSS) as terminating/copolymerizing agent to introduce the branching points. CDMSS was slowly added to living PS chains to prepare the first-generation macroinitiators, which were then used to grow the second-generation PS chains, which were again

Scheme 34. Preparation of Dendrimer-Like Highly Branched Polymers by a Convergent Approach[369]

Scheme 35. Examples of an Oligo-inimer and *AB₂* Macromonomers
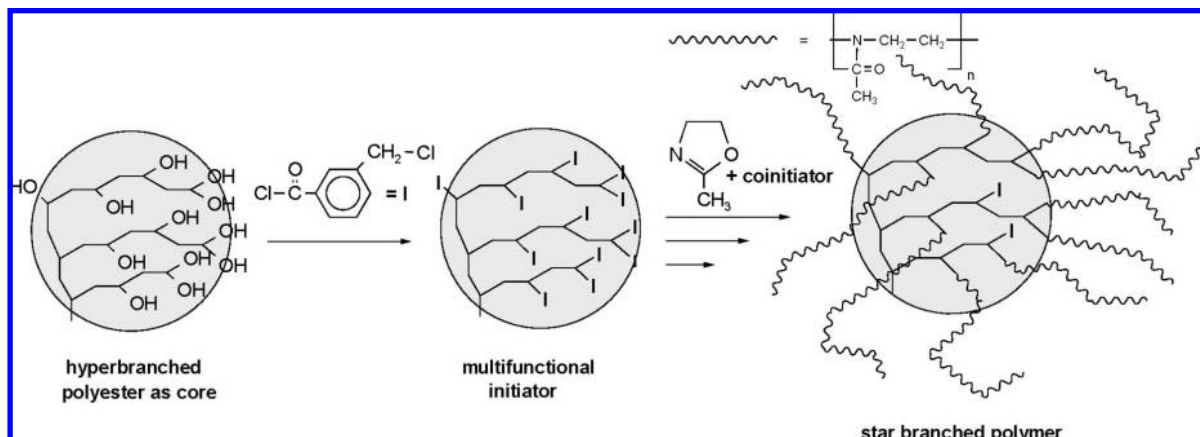

reacted with CDMSS (Scheme 34). Hadjichristidis and co-workers resorted to a similar approach to assemble anionically dendrimer-like homo- and copolymers of styrene and isoprene, e.g., also using CDMSS as a branching agent in combination with multifunctional cores.[380]

The macromonomer approach (Scheme 33) was applied by Hutchings and colleagues[370] as the third major method to this class of polymers. These authors designed α,ω,ω-trifunctional macromonomers based on polystyrene (Scheme 35) and used them as *AB₂* building blocks either in polycondensation with[370] or without[381] core moieties, leading to polystyrene with ether branching sites called "Hyper-Macs" or "Dendri-Macs." *ABₓ* monomers based on ROP chemistry have been also reported by Hedrick[263] (Scheme 35) and Hong.[362] This concept also includes the use of "macroinimers" applying SCVP as reported by Hazer,[125] Tsukruk et al. (employing a RAFT ethyleneglycol–polystyrene mac-

roinimer),[382] and Wooley et al.,[258] who reported on the use of an "oligoinimer" (Scheme 35).

Anionic polymerization was used to prepare silane-end-functionalized polybutadiene and polyisoprene macromonomers with different molecular weights.[123,383] These *ABₙ* macromonomers were polymerized by a hydrosilylation reaction in bulk to obtain branched polymers, using Karstedt's catalyst. Furthermore, it was possible to introduce a variety of functional silanes without increasing the overall number of reaction steps by a convenient *AB₂ + A* type "pseudo-copolymerization" method.

AB₂ type monodisperse conjugated oligomers carrying two bromo functional groups and one boronic ester functional group were prepared by iterative deprotection and Sonogashira cross-coupling reactions.[384] Suzuki polycondensation of these *AB₂* type monodisperse oligomers afforded hyperbranched polymers. The prepared hyperbranched conjugated

Scheme 36. Grafting-from Approach for hb-Core Star Copolymers Exemplified by the Cationic Grafting of Methyloxazoline from a Modified hb Polyester Core[400]

polymers possessed not only precisely controlled conjugation length like monodisperse conjugated oligomers but also the structural feature of hyperbranched polymers.

An interesting starlike block-copolymer structure with improved ionic conductivity was reported recently by Peng et al.[385] Here, highly branched polyglycidol "chain ends" were grafted from a polystyrene four-armed star structure having OH functional end groups.
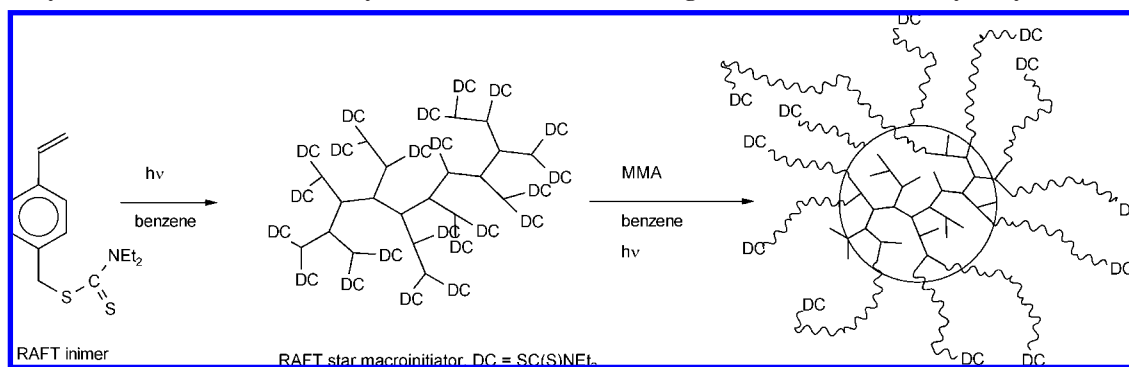
2.3.3. Linear-Hyperbranched Hybrid Structures

The combination of linear chains and dendritic architectures was extensively studied early on for perfectly branched dendrons leading to complex architectures, e.g., dendron-linear block-copolymers[386,387] and dendronized or monodendron jacketed linear polymers,[388–390] and to star polymers[391–393] with a dendritic core. Especially the attachment of monodendrons to a linear polymer chain by postmodification or by polymerization of monodendron-containing macromonomers has attracted much attention due to the visualization of these stiffened polymer chains as single nanoscopic macromolecules by AFM.[388,390,394,395] The strongly expanded field of dendronized polymers as cylindrical-shaped giant macromolecules and nanoscopic objects covering improved synthesis methods has been recently summarized by Schlüter[396] and by Frauenrath.[397]

Star-hb Core Structures Leading to Core–Shell Type Materials. The preparation of more complex architectures using hyperbranched macromolecules, however, is a more recent trend. The field of star polymers with a hyperbranched core has been an area of particular interest.[41,54,398–401] Free radical, controlled radical, ring-opening, anionic, and cationic polymerizations have been applied using hyperbranched macroinitiators. The resulting polymers show typical behavior of star polymers, e.g., low solution viscosities nearly independent from molar mass. By combination of suitable core/arm combinations, structures with amphiphilic properties can be obtained. Scheme 36 depicts the general scheme of the hb macroinitiator approach for hb core-star polymer exemplified by an early example of star polymers with a relatively nonpolar hyperbranched polyester core and polar poly(methyloxazoline) arms prepared though cationic polymerization.[400] Wang et al.[402] used this approach to produce electrically conducting star polythiophene polymers from hyperbranched polyphenylene core modified with bromothiophene units.

Today, a vast variety of often complex star-type structures have been prepared based on hyperbranched cores mainly through the hb macroinitiator or core-first approach. In addition to hb polyesters cores, which have been used as initiators for ATRP[403] and ROP,[404] the most often employed core moieties are hyperbranched polyethers, like hb polyglycerol, which are used as multifunctional initiators for various homo- and block-copolymer arms (poly-ε-caprolactone, PS, PS-b-PtBA).[405–407] This approach allowed the making of materials with high biocompatibility,[405] with thermoresponsive behavior,[408] or with arms containing photoactive azobenzene units[409] or mixed functionality.[410]

The hb poly(ethylene imine) shows also high potential for the preparation of core–shell-type star polymers. Baumann et al.[411] grafted linear polyamide-12 onto hb PEI in two different ways, as ring-opening polymerization of laurolactam and through transamidation of linear PA12 in the presence of core PEI molecules. Both methods provided almost uniform materials. PEI was used also as a multifunctional macroinitiator for the ring-opening polymerization of lactide.[412] In contrast, pH-responsive dendritic core–shell nanocarriers for polar dyes were prepared by linking a biocompatible PEG shell to hyperbranched PEI cores with pH-responsive linkers, which is considered a rare example of the arm-first approach in the hb star synthesis. In order to create a dense shell, three PEG chains were attached to the core through one linker molecule.[43] PEI was also used as multifunctional initiator for the NCA polymerization of γ-benzyl-L-glutamate, resulting in an amphiphilic star-type structure with a polypeptide shell.[413]

Various cores prepared by SCVP have been applied as hb macroinitiators, e.g., for ROP of CL,[414] photo-RAFT of (methyl)acrylates (Scheme 37),[415] cationic polymerization of isobutylene,[416] or the preparation of block-copolymers arms.[417] The later materials could be transformed into conductive core–shell nanoparticles. The degenerative transfer polymerization of p-(iodomethyl)styrene was also successfully applied to prepare directly iodomethyl-terminated macroinitiators suitable to initiate the polymerization, e.g., of styrene and tBuA and also to prepare block-copolymer arms.[418,419] Dworak and co-workers[420] reported also a grafting-onto approach by attaching living polyether macroanions onto a chloromethyl terminated hb core prepared by SCVP of p-(chloromethyl)styrene to obtain amphiphilic core–shell-type PEO stars.

Scheme 37. Synthesis of a hb-Core Star Polymer Based on Self-Condensing UV-Initiated RAFT Vinyl Polymerization[415]

A new method for the synthesis of starlike aliphatic polyesters with hyperbranched cores, which does not fit in the schemes of hb macroinitiator (core-first) or arm-first approaches, has been developed by Biela and Polanczyk.[421] By reacting living linear polyester precursors, poly(CL) and poly(LA) with bislactones branched architectures could be realized. The method requires the selection of reaction conditions under which the produced hyperbranched structures can be kept in solution without gelation. By the adjustment of the precursor molar mass and the ratio of the precursor active center concentration to the concentration of bislactone, highly branched polyesters with different topologies were created including starlike products. Similarly, the anionic polymerization involving functionalized diphenylethylenes[104] or chlorosilane moieties[380] outlined under the chain-growth approaches is also suitable to prepare complex branched structures including starlike macromolecules.

In addition, rather complex architectures were prepared involving hb cores or similar highly branched structures. As example, the synthesis of special arborescent star-type block-copolymers composed of rubbery polyisobutylene and glassy polystyrene blocks was accomplished by the use of arborescent polyisobutylene macroinitiators, prepared by the use of 4-(2-methoxyisopropyl) styrene inimer in cationic polymerization.[422] Hawker and Qiao reported dendron functionalized core cross-linked star polymers.[423] Novel thermoresponsive shell cross-linked three-layer onion-like polymer particles were prepared using hyperbranched polyglycerol (PG) as the parent compound.[424]

Linear-Hyperbranched Block Copolymers. In comparison to the perfectly branched dendritic structures, where often dendrons are combined with linear polymer chains either as end "groups" (*AB* or *ABA* block-copolymers, nicely reviewed recently by Gitsov[425] and also Cho[426]) or in dendronized polymers,[396,397,425] only a few examples exist so far on linear-hyperbranched block-copolymer structures. The main reason for that is that the less controlled synthetic approaches toward hb structures easily can lead to undesired side reactions in block-copolymer formation, which reduces the control of the structure and can result in mixtures of products.
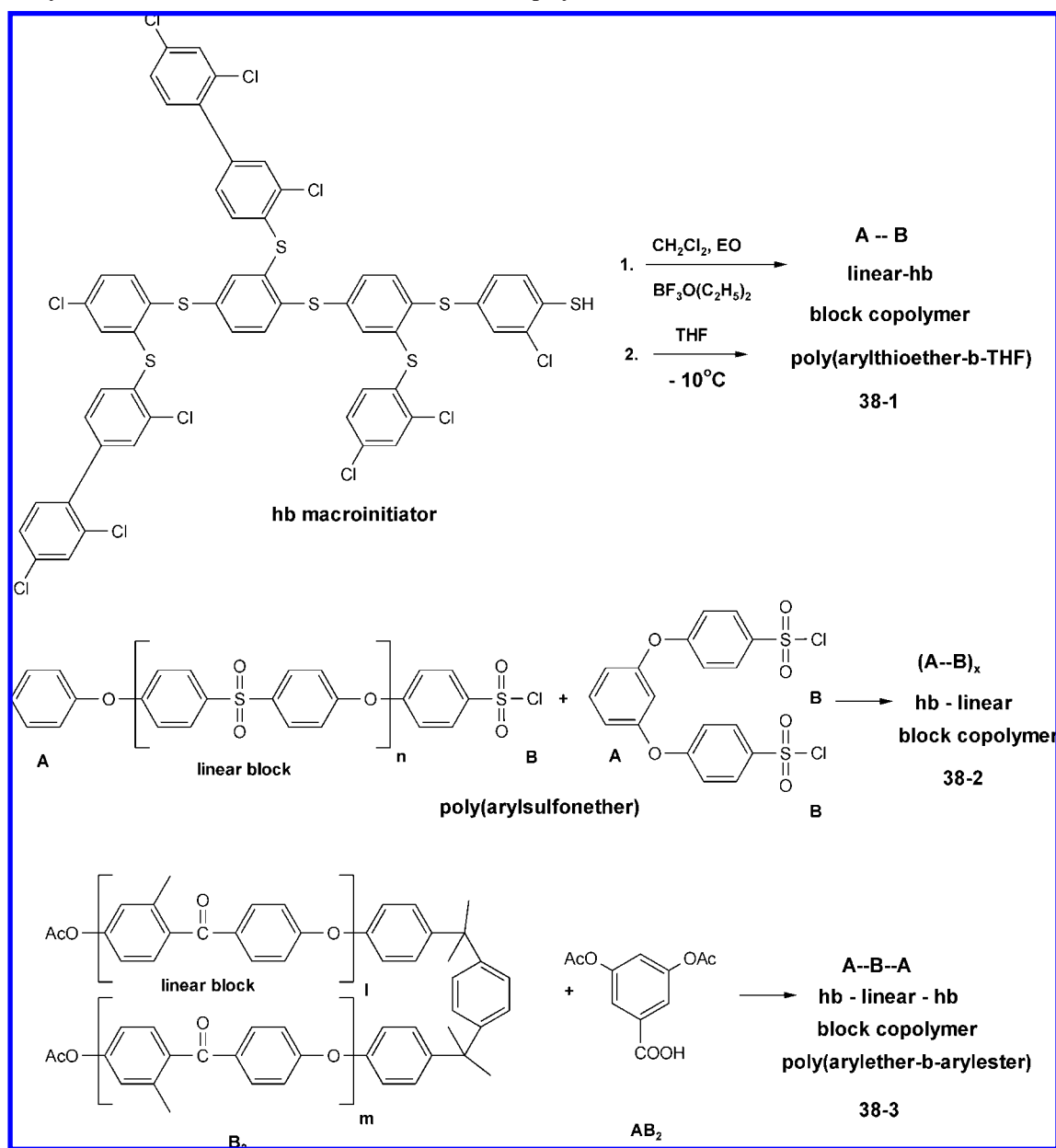
One early example is a triblock-copolymer *A*−*B*−*A* with *A* consisting of hyperbranched polyesters from 3,5-dihydroxybenzoic acid and *B* being an oligo(etherketone) as reported by Kricheldorf et al.[427] The triblock was prepared by copolycondensation of the telechelic linear oligomer with *AB₂* monomers (Scheme 38). The polymer proved to be fully soluble in THF due to the hyperbranched structural components.

Linear-hyperbranched block-copolymers, in which linear polytetrahydrofuran (PTHF) is linked to the focal unit of

hyperbranched poly(phenylene sulfide) (HPPS-SH), have been synthesized by condensation polymerization of 2,4-dichlorobenzenethiol, subsequent transformation of the resultant HPPS-SH to HPPS−OH, and then initiation of the cationic ring-opening polymerization of tetrahydrofuran (THF) using HPPS−OH as a macrotransfer agent (Scheme 38).[428] Interesting linear-hyperbranched poly(ether sulfone) block-copolymers have been prepared by Kakimoto et al.[429] in a two-step manner. First, in an one-pot synthesis, the *AB* monomer was polymerized to generate a linear poly(ether sulfone) *AB* oligomer followed by addition of the *AB₂* monomer in a large excess (19:1, *AB₂/AB*) to generate the hyperbranched block (Scheme 38). Recently, Osano and Turner reported on linear poly(ether sulfone)s PES with dendritic terminal groups on both sides using arylether ketone dendrons of first and second generations as monofunctional end-cappers in the step-growth polymerization of 4,4-difluorodiphenylsulfone and bisphenol A.[430] By that, it was possible to reduce the high shear melt viscosity of PES without affecting the stress−strain properties.

Frey et al.[431] developed a three-step strategy for the preparation of well-defined amphiphilic, linear hyperbranched poly(styrene-*b*-hb glycerol) block-copolymers by "hypergrafting". The synthetic procedure is based on a combination of carbanionic polymerization with the alkoxide-based, controlled ring-opening multibranching polymerization of glycidol. A linear *AB* diblock-copolymer polystyrene-*block*-polybutadiene was obtained by anionic copolymerization. Subsequent hydroxylation by hydroboration led to PS₅₀₈-*b*-(PB−OH)₅₆, used as macroinitiator for the polymerization of glycidol under slow monomer addition conditions (Scheme 39). A similar strategy was reported by the same group[432] for poly(styrene-*b*-hb-carbosilane) block-copolymers based on (PS-*b*-PB) diblock-copolymers with a short, functional 1,2-PB block. The functional polybutadiene block was used for the grafting of branched *AB₂*-type carbosilane monomers. Biocompatible, double hydrophilic linear-hyperbranched block-copolymers based on poly(ethylene oxide) (PEO) and hb poly(glycerol) consisting exclusively of an aliphatic polyether structure were prepared from linear PEO-*b*-(*l*-PG) precursor block-copolymers, obtained via anionic polymerization of ethylene oxide and subsequently ethoxyethyl glycidyl ether (EEGE).[433] In order to generate initiating functionalities for glycidol, the protected hydroxyl groups of the P(EEGE) block were recovered by hydrolysis with hydrochloric acid. Partial deprotonation of the linear poly(glycerol) block with cesium hydroxide permitted "hypergrafting" of glycidol onto the alkoxide initiating sites, using the slow monomer addition technique.

Scheme 38. Synthesis of Various Classes of hb-Linear Block-Copolymers

Direct growth of hyperbranched polymers on both ends of a linear polymer was reported recently by Wan and Pan.[434] Control of hyperbranched chain growth on both ends of PEO has been achieved in the ATRP of an inimer, 2-((bromobutyryl)oxy)ethyl acrylate, using a bifunctional PEO macro-RAFT agent (Scheme 40). The principle of this synthetic strategy is interrupting propagation of the hyperbranched chain radicals by transforming the active species of their chains onto the terminal functional group of linear PEO. In this reaction, propagation of hyperbranched chains is restricted, and the probability for propagation from the end of PEO increases.
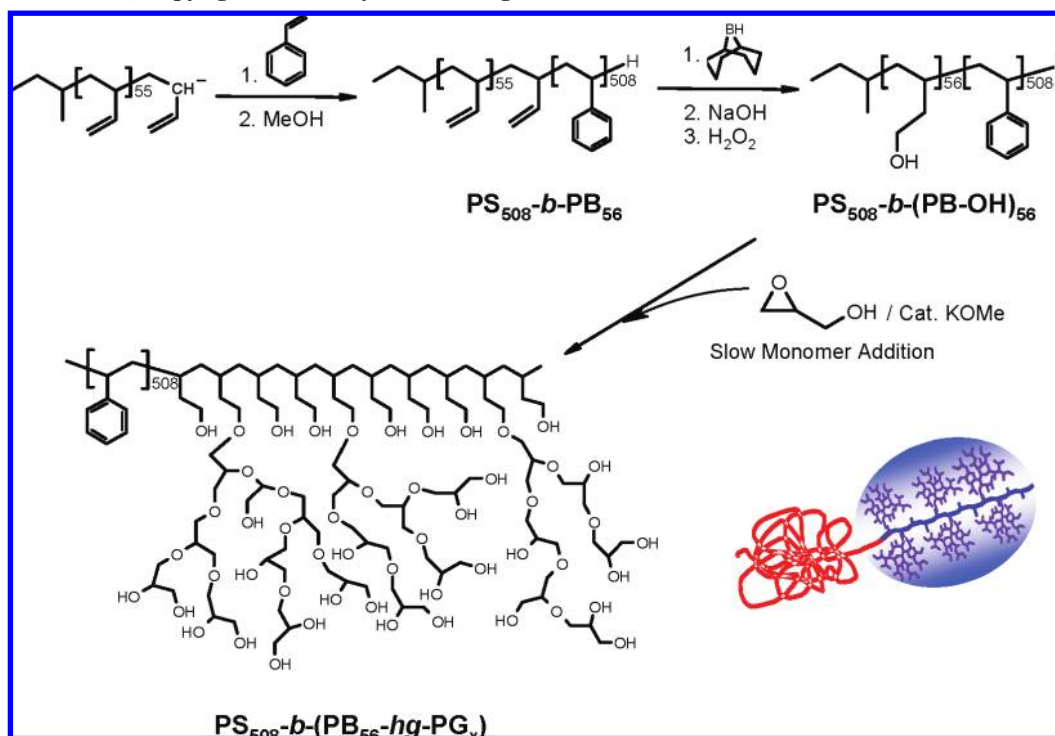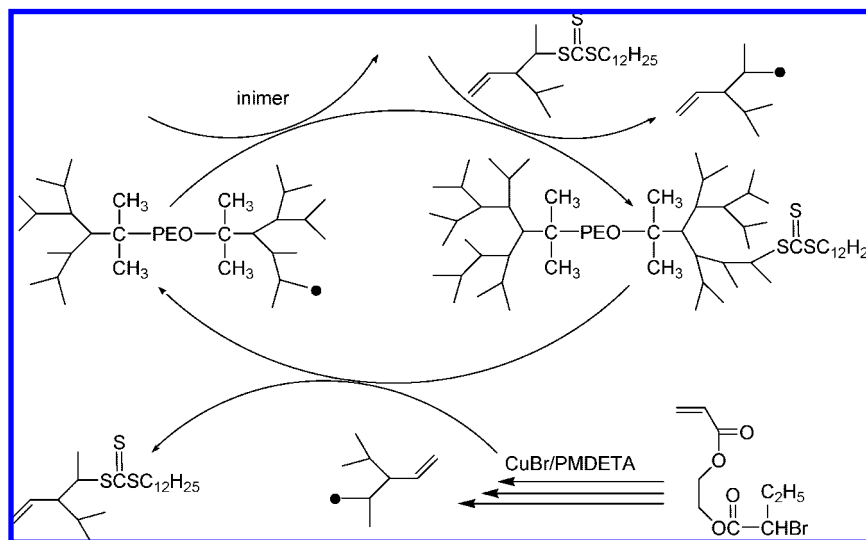
Very recently, for the first time, a hyperbranched "dendronized" homopolymer has been reported, prepared through hb macromonomers in a one-pot synthesis.[435] The strategy employed the simultaneous cationic polymerization of 4-acetoxystyrene in combination with the hyperbranched polymerization of 3,5-diacetoxybenzoic acid, a reversible transes-

terification process under thermal conditions (Scheme 41). Here, the full mechanism of the reaction still has to be explored.

2.3.4. Core—Shell Structures, Nanocapsules, Self-Assembly

As already indicated, polymer starlike architectures with hyperbranched cores can exhibit core—shell type topography, often with an amphiphilic character that allows consideration of these macromolecules as nanocontainers.[43,105,436]

A core—shell-like architecture can be achieved by considering the hb starting part as core and the grafted arms as shell provided that core and shell are immiscible and show different polarity character. Thus, fragrance molecules had been encapsulated into a core—shell structure with a nonpolar core based on Boltorn and PCL arms.[436] An amphiphilic biodegradable star-shaped polymer was conveniently prepared by ring-opening polymerization of CL with hyper-
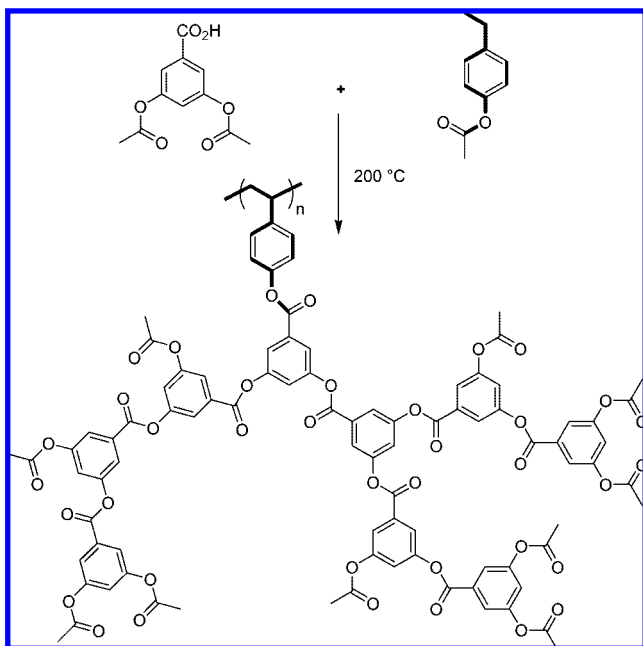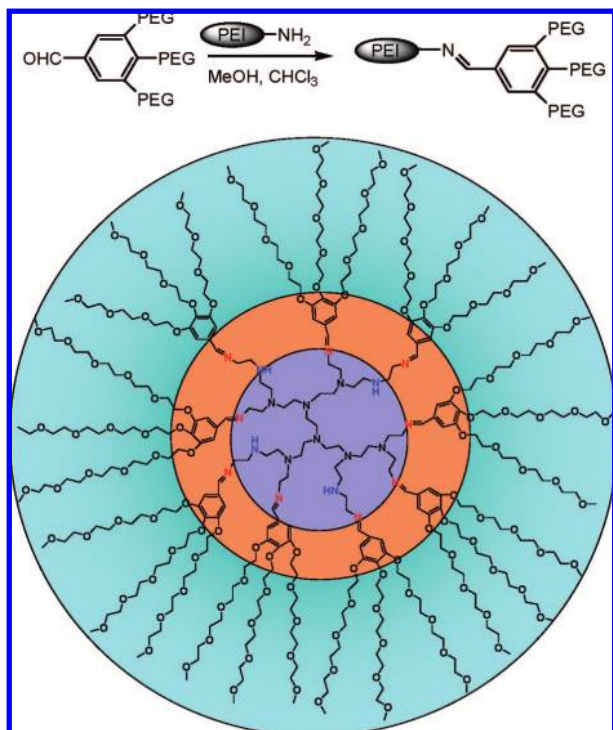
Scheme 39. Linear-hb Block-Copolymer through Hypergrafting of One Block (Scheme Provided by H. Frey; Reprinted with Permission from Ref 431; Copyright 2005 Wiley-VCH Verlag GmbH & Co. KGaA)

Scheme 40. Synthesis of hb-Linear-hb Block-Copolymers through SCV RAFT Polymerization[434]

branched poly(ester amide) (PEA) as a macroinitiator. Because of the hydrophilic PEA core and hydrophobic PCL shell, the obtained star polymers displayed inverted unimolecular micellar structure and were able to transport polar dyes from water to the organic phase with a high efficiency. Also, the starlike structures prepared by the Haag group[43,437] based on hyperbranched PEI cores and biocompatible PEG shells (Scheme 42) have been used as nanocarriers for studying the encapsulation and transport of polar dyes as well as therapeutics and diagnostic agents. Because of the incorporated acid-labile junctions, in the core−shell-like molecules, controlled release of the polar dyes was observed under acidic conditions.

Starlike structured polymers having N-isopropyl acrylamide and N,N-dimethylaminoethyl acrylate block-copolymer arms and a polyglycerol core were further cross-linked in

the shell to obtain thermoresponsive 3-layered nanoparticles.[424] Chu and co-workers[417] reported electrically conductive core−shell nanoparticles from multiarmed poly(n-butyl acrylate-b-polystyrene) (PBA-b-PS) starburst block-copolymers. The outer PS shell of the star copolymer was converted into hydrophilic poly(p-styrenesulfonate) with acetyl sulfate to generate amphiphilic PBA-b-poly(p-styrenesulfonate) unimolecular micelles. Finally, the oxidative propagation of 3,4-ethylenedioxythiophene (EDOT) on the PSS chains was carried out by counterion-induced polymerization to produce a stable aqueous dispersion of star-shaped PBA-b-PSS/PEDOT complex, which could be visualized as a conducting core−shell nanoparticle.

Even more pronounced core−shell structures are achieved in the dendrimer-like polymers prepared through the divergent approach, when amphiphilic block-copolymer structures

Scheme 41. One-Pot Synthesis of a Hyperbranched Graft Homopolymer[435]

Scheme 42. Synthesis of pH-Sensitive Core−Shell-Like Nanocarriers by the Grafting of Dense Shell of PEG Chains onto hb PEI Core (Scheme Provided by R. Haag; Reprinted with Permission from Ref 437; Copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA)

are created. By this technique, for example, Gnanou et al.[438−440] prepared dendrimer-like polymers composed of an inner PEO core and an outer PS or poly(acrylic acid) shell, but also the inverse architecture, e.g., with a hydrophobic PS generation covered by a hydrophilic PEO shell, was achieved. Recently, the same group further functionalized the interior of core−shell structures by incorporation into dendrimer-like PEO pH-sensitive poly(acrylic acid) branches that had been localized at the branching junctions (Scheme

43).[441] In a different approach from the same group, it was even possible to prepare Janus particle-type dendrimer-like poly(ethylene oxide).[442]

A tandem polymerization methodology—chain-walking polymerization followed by atom-transfer radical polymerization—was developed for the efficient synthesis of nanoparticles for bioconjugation.[443] The chain-walking palladium catalyzed methodology was used to prepare dendritic polyolefins bearing multiple initiation sites, which were used as macroinitiators for subsequent ATRP. Addition of an N-acryloyloxysuccinimide (NAS) monomer at the end of the ATRP afforded NAS-activated polymer nanoparticles. Conjugation with both small dye molecules and protein yielded nanoparticle conjugates with relatively high dye or protein per particle ratio (Scheme 44).

Self-assembly aspects play an increasingly important role in the area of functional nanomaterials, which has been comprehensively summarized by Smith for dendritic building blocks.[158] Thus, the concept of self-assembly was early on used also for the preparation of hb polymers as demonstrated by Reinhoudt et al.[157] (see Scheme 10) using an organopalladium methylcyano AB_2 complex. Large organopalladium spheres with diameters of approximately 200 nm were obtained by this approach.

Self-assembly can also be used to create even larger structures from preformed hyperbranched macromolecules. Thus, aggregation into large spherical micelles of >100 nm was observed for amphiphilic hyperbranched multiarm copolyethers of poly[3-ethyl-3-(hydroxymethyl)oxetane]-star-poly(propylene oxide).[444] Macroscopic self-assembly of hyperbranched polyesters was achieved by substitution of the terminal hydroxyls of a hb polyester core with benzoyl chloride. It has been found that well-defined macroscopic, even rodlike, structures can be formed via hydrogen bonding and $\pi-\pi$ stacking interactions. The macroscopic molecular self-assembly of an amphiphilic hyperbranched copolymer in acetone generated multiwalled tubes millimeters in diameter and centimeters in length. The thickness of the tube walls approaches 400 nanometers, and the walls have an inhomogeneous lamella structure that alternates between ordered hydrophilic domains and amorphous, partly irregular hydrophilic domains.[445]

On the other hand, hyperbranched structures can also be further modified or functionalized through noncovalent interactions. By this process, e.g., a new class of crystalline inclusion complexes of a multiarm hyperbranched polyether combined with various cyclodextrins was successfully prepared,[446] and the above-mentioned preparation of conductive nanoparticles[417] relies also on the noncovalent interactions of the outer PSS shell with the EDOT monomer.

Compared to other materials used for functional nanomaterials, like perfectly branched dendritic building blocks or well-defined amphiphilic block-copolymers, self-assembly concepts in combination with the irregular hyperbranched structures are still rarely and only very recently explored. Nevertheless, the first examples reported to date demonstrate well that this class of materials holds high promise.

3. Characterization of Hyperbranched Polymers

The enormous synthetic development in the field of hyperbranched polymers in the last two decades is based on the fact that these compounds possess new, particular characteristics that strongly influence material properties and open new application fields.[3,5−7,447] Therefore, simultaneously

Scheme 43. Schematic Representation of pH-Sensitive Dendrimer-like PEO of Generation 5 Functionalized by 21 Branches of PAA at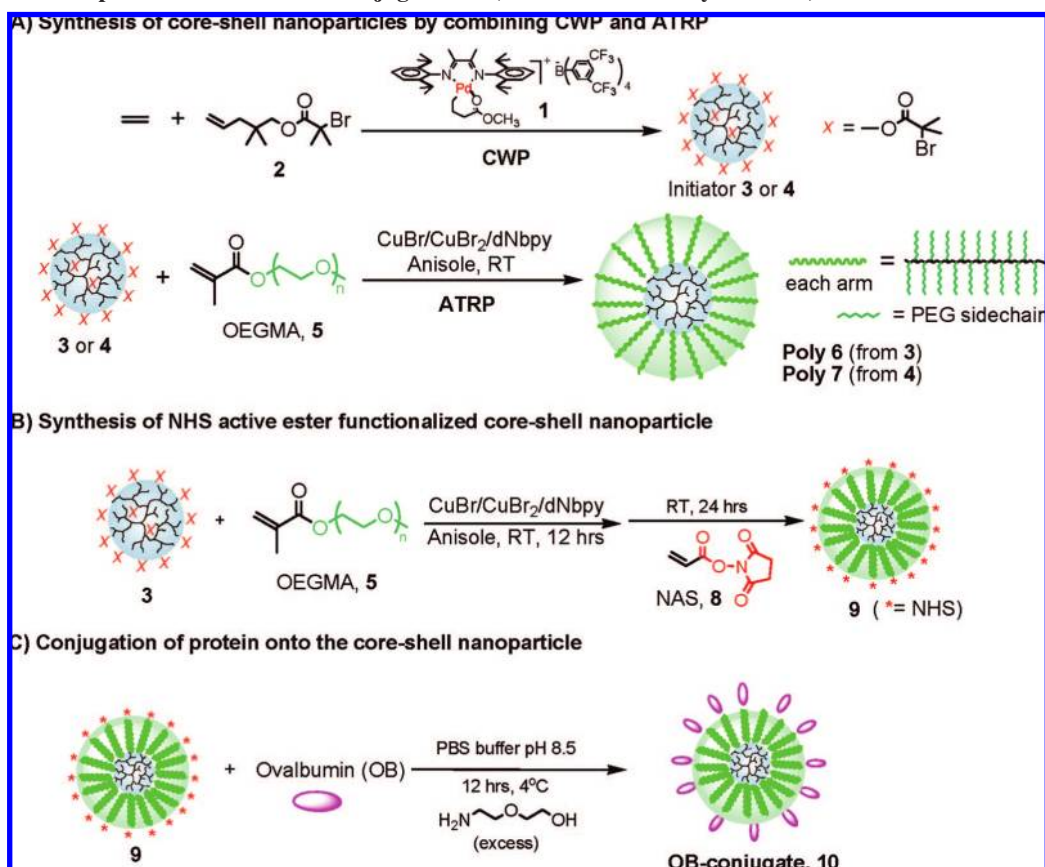 the Branching Points within the Dendritic Scaffold up to Generation 4 (Scheme Provided by Gnanou and Taton; Reprinted with Permission from Ref 105; Copyright 2007 Royal Society of Chemistry)

Scheme 44. Preparation of Core−Shell Nanoparticles by Combining Chain-Walking Polymerization (CWP) and ATRP, Followed by End Group Modification and Bioconjugation[443] (Scheme Provided by Z. Guan)
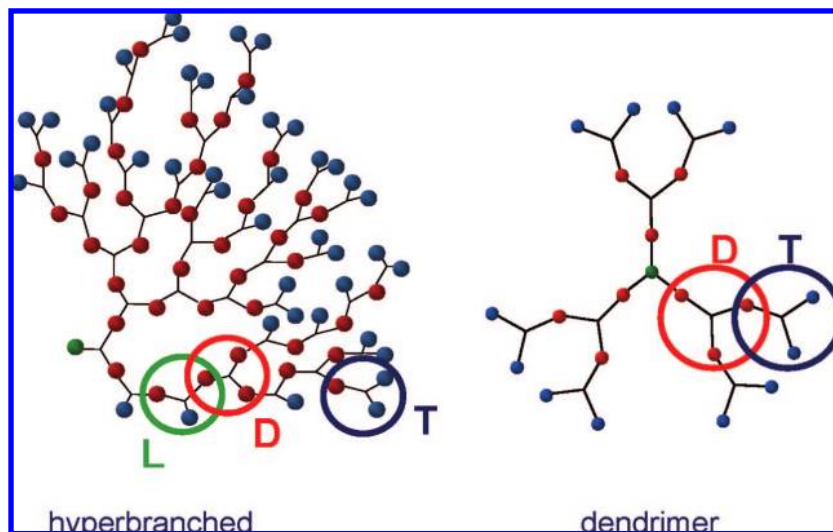

to the synthetic progress, strong efforts have been made to characterize, understand, and theoretically describe the properties of the hyperbranched polymers in order to obtain reliable knowledge about their structure−property relationships. Considerable progress on the fundamental structure−property relationships in hb polymers has been achieved since the theoretical predictions made in the middle of the 20th century concerning polymers from AB_x monomers.[25,77] The increased availability of a wide variety of hyperbranched polymers, on the one hand, has enabled the verification of Flory's predictions but, on the other hand, has also revealed deviations in real systems from the assumptions that had been made by Flory for ideal AB_x systems. In addition, the complex branched hb polymer structures have presented an

enormous challenge for full structure characterization and have shown limitations of current techniques.

On the basis of many detailed studies, we certainly have enhanced our knowledge about the characteristics of hyperbranched AB_x type as well as $A_2 + B_y$ polymers, branched structures achieved by SCVP, and, in general, of different highly branched polymer architectures. There are several excellent reviews describing the topic of characterization of these materials by the groups of Müller,[32] Long,[53] McLeish,[448] Gauthier,[358] Jikei,[449] and Burchard.[127] All this work shows that hyperbranched polymers are very complex structures with multidimensional, broad distributions, e.g., in molar mass, degree of branching, or chemical structure. They have unique solution and bulk properties that differ

Scheme 45. Schematic Representation of the Different Polymer Units in Hyperbranched Polymers Compared to Dendrimers: L = Linear; D = Dendritic; and T = Terminal Units

strongly from those of linear and star or less branched polymers. In this part of the review, the most significant insights into the molecular properties of the hyperbranched polymers are collected and discussed. An overview of the different methods for their structural, thermal, solution, and bulk characterization will be given and their potentials and limits will be discussed. In the discussion, a comparison of the experimental methods for characterization with theoretical results and simulations will be integrated. Most of the analysis of the hyperbranched polymers is based on the property correlation to linear structures or to 100% branched molecules, in order to understand the differences and thus, the influence of the randomly branched architecture on the characteristics of these macromolecules.

3.1. Structural Characterization

3.1.1. Degree of Branching

The degree of branching (DB) is one of the most important parameters of hb polymers, because of the fact that it is directly correlating with the density of the polymer structure and the number and location of the end groups. In contrast to perfectly branched dendrimers, which possess only dendritic and terminal units, the hb polymers incorporate additionally linear units. Theoretically,[77] in the case of the ideal statistical self-condensation of an AB_2 monomer, which means equal reactivity of all B groups and no side reactions like cyclization, the number of the linear units should occupy
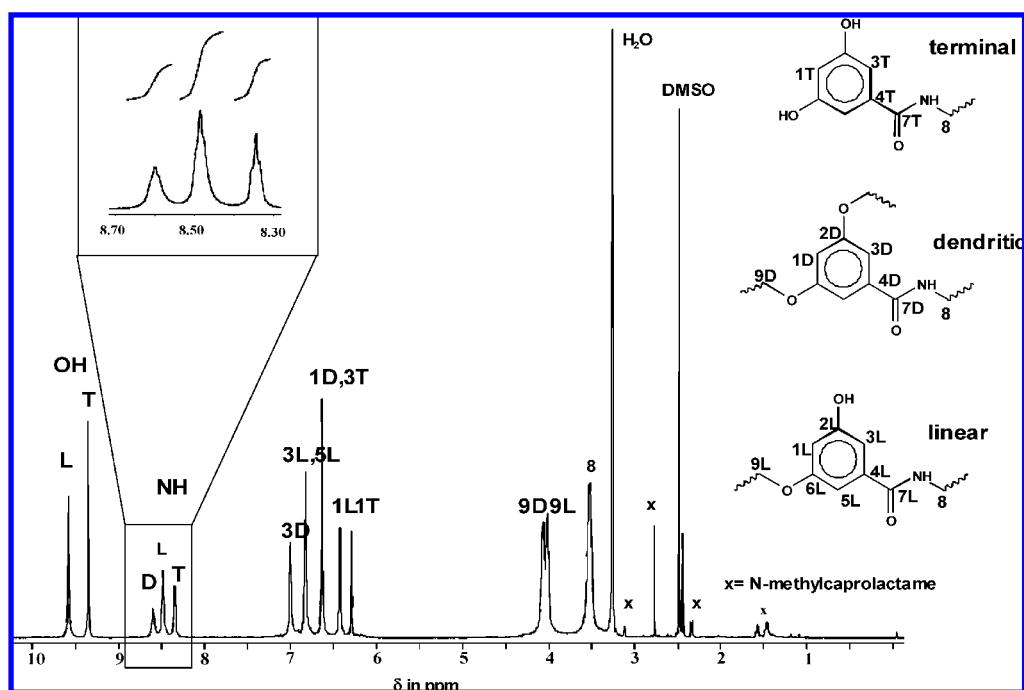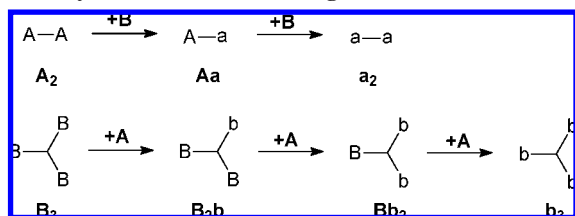

Figure 1. ^{1}H NMR spectrum for determination of the amount of T, L, and D units in hyperbranched poly(etheramide) made by ring-opening polymerization of an AB_2 monomer (**13−2**) according to Scheme 13.[199] Adapted with permission from ref 199. Copyright 1999 Wiley VCH.

Scheme 46. Possible Reactions of the Functional Groups in $A_2 + B_3$ Systems and the Resulting Structural Units

50% and the dendritic units only 25% of all structural units, as shown in Scheme 45.

The ratio of the structural units can be determined by NMR measurements as described in Figure 1 for the example of hb poly(etheramide).[199] This polymer is a product of an AB_2 monomer, and the definition and assignment of the different structural units is straightforward.

The definition and determination of the terminal (T), linear (L), and dendritic (D) units after reaction of $A_2 + B_y$ is more complicated. The characterization of this type of hb polymer is described in several detailed investigations.[98,83,89,310,450] Nevertheless, the NMR analysis of these structures is not trivial, and a number of possible monomer combinations have to be considered as described in Scheme 46 for an $A_2 + B_3$ reaction. The NMR analysis of these structures mostly requires the use of model compounds.[89,98,310] An example of the ^{13}C NMR analysis of the different structural units of polyphenylene synthesized from $A_2 + B_3$ in different ratios is shown in Figure 2.[83]

The calculation of the DB for AB_2 type of hb polymers using the values for T, D, and L was described in the 1990s in the work of Kim and Webster[451] and Fréchet et al.[62] as a function of the ratio of the dendritic (D), terminal (T), and linear (L) units as

$$DB_{Fréchet} = \frac{T + D}{T + D + L} \quad (1)$$

In the case of perfect dendritic branching, i.e., dendrimers, the DB = 1. Taking into account that $T = D + 1$, according to eq 1, even fully linear structures would possess a DB > 0. This definition can indeed accurately describe DB for products with higher polymerization degrees, where the number of the dendritic units is approximating the number of the terminal units, but in the low molar mass region, another equation suggested by Frey et al.[452] and Yan et al.[118] is more suitable for the calculation of the DB:

$$DB_{Frey} = \frac{2D}{2D + L} \quad (2)$$

For determination of the DB of copolymers of type $A_2 + B_3$, the different structural units of Scheme 46 have to be taken into account. In this case, the dendritic groups are of type b_3, which have three reacted functionalities, the Bb_2 groups would be the linear units with two reacted functionalities, and the B_2b group is the terminal unit:[94]

$$DB = \frac{2D}{2D + L} = \frac{2(b_3)}{2(b_3) + (Bb_2)} \quad (3)$$

The usual way in dendritic chemistry to describe the DB by eqs 1 and 2 does not directly correlate with the well-established number of branches per 1000 monomer units, N_{1000}, from the analysis of the randomly long-chain branched

polymers. For this reason, the concept of branch point fraction (FB) has been introduced[32] as

$$FB = \frac{D}{2D + L} = \frac{1}{2}DB = \frac{1}{1000}N_{1000} \quad (4)$$

Use of eq 4 makes it possible to rank dendritic polymers as a branched polymer structure, but nevertheless the specific, pure dendritic topology is not comparable to the long-chain branched or star branched polymers, where the physical properties are still governed by macromolecular entanglements. Even topologies like arborescent polymers or combinations of linear and hb structures in one molecule are not directly comparable to the long-chain branched polymers.

In order to control the branching degree, extensive investigations on AB_x as well as on $A_2 + B_y$ systems have been carried out. The tuning of this property is certainly limited due to the statistical nature of the reaction. Nevertheless, there are special reaction procedures for AB_x hb polymers like the process described in the previous sections as slow monomer addition.[73,74] In the case of $A_2 + B_3$ reaction, high sensitivity of the degree of branching on the ratio of the monomers as well as on the sequence of the monomer addition was experimentally observed and simulated.[84,450,453] The simulations by Schmaljohann[84] showed that, at 1:1 ratio of A_2/B_3, a strong difference could be observed depending on the sequence of monomer addition. Applying simultaneous stepwise addition of A_2 and B_3, a DB = 0.65 could be achieved, compared to the stepwise addition of B_3 to A_2 solution, which leads to a DB = 0.91.

A further possibility to control the branching degree in hb polymers is the copolycondensation of multifunctional AB_x with bifunctional AB monomers.[26,53,281,360,361] A combination of an inimer and a comonomer in SCVP leads as well to reduced branching.[32] These two synthetic procedures were already described in sections 2.2.4 and 2.3.1. The determination of the degree of branching in such copolymer systems was investigated in depth by Frey and Hölter[454] using calculations based on conversions of the different functionalities. For a self-condensing $AB_2 + AB$ system, the DB can be described simply by the following equation:

$$DB = \frac{2D}{2D + L_{AB_2} + L_{AB}} \quad (5)$$

By combining AB_2 with bifunctional AB monomers, e.g., in polycondensation, the degree of branching can be well-adjusted, as shown in the work of Schallausky et al.[281] Figure 3 shows the ratio $r_p = [AB]/[AB_2]$ of the monomer units indicated by ^{13}C NMR and the ratio $r_m = [AB]_0/[AB_2]_0$ in the feed reaching a full incorporation of the monomer into the hb polymer, leading to a constant reduction of the DB. Unfortunately, in this case, it was not possible to achieve a linear product from the AB monomers due to cyclization reactions in the early stage of the reaction. Nevertheless, other authors successfully covered the polymer architecture from completely linear up to hyperbranched, and they report similar results.[32,255] However, the agreement between r_m and r_p has not always been observed to be good due to different reactivity of the comonomers. In the case that a nearly linear structure is attempted, i.e., $r_p \gg 1$, the DB could be described using[32]
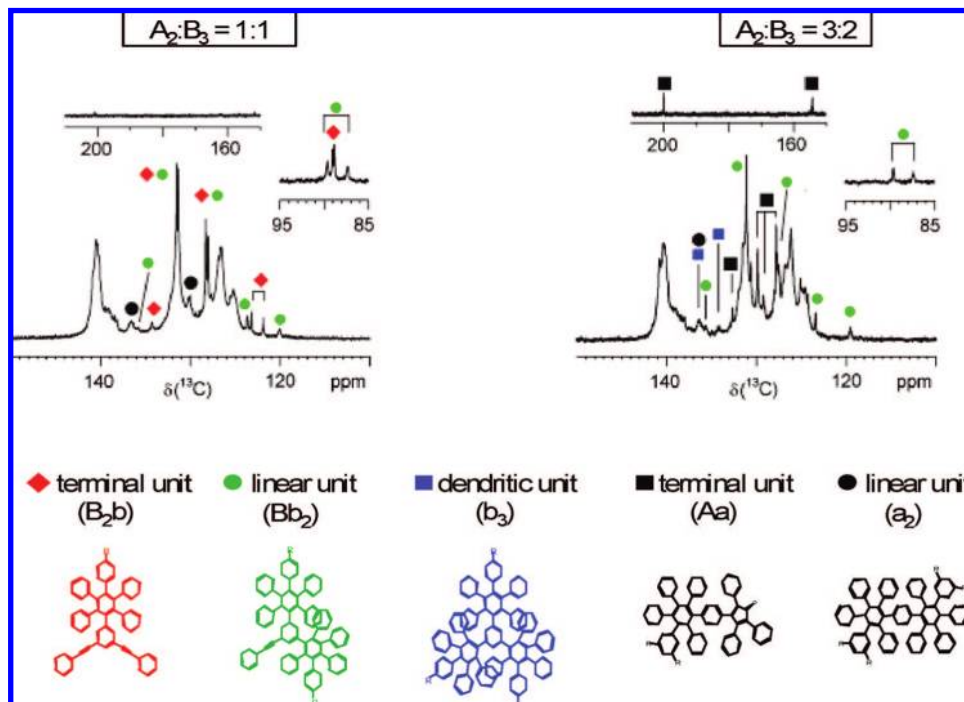
Figure 2. ^{13}C NMR spectra and different structural units of polyphenylenes produced by different ratios of $A_2 + B_3$ monomers (compare Scheme 16).[83]
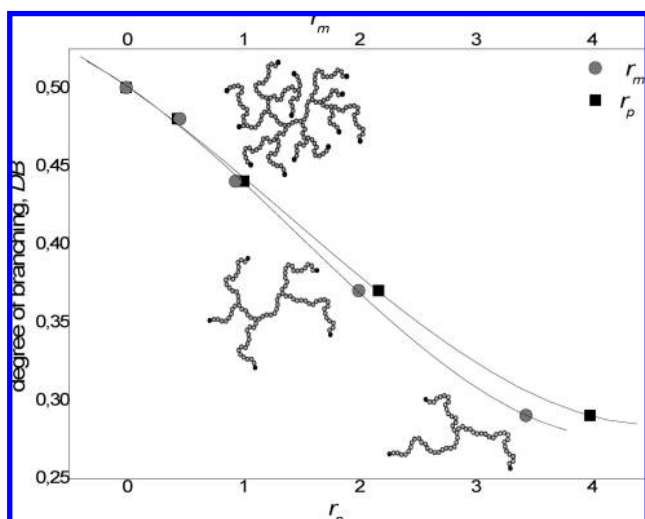

Figure 3. Dependence of the degree of branching on the AB/AB_2 ratio in the feed (r_m) and in the resulting polymer (r_p) for an hb polyester.[281]

$$\text{DB} = \frac{2}{2 + r_p} \approx \frac{1}{r_p} \qquad (6)$$

The development of the degree of branching during the reaction in the ideal case, as described by Flory,[77] is independent from the degree of polymerization. However, even in polycondensation systems, which are described as fully statistical,[16] a dependence of the degree of branching on the progress of the reaction has been observed. Such kinetic investigations were carried out on aliphatic–aromatic polyesters, applying detailed interpretation of ^{13}C and ^{1}H NMR measurements. In this way, a strong increase of the degree of branching from DB = 0.06 up to 0.40 during the early stage of the polymerization (DP = 1 up to 8) has been determined using the Frey equations.[454] However, at high conversion of the A-group, a degree of branching of DB =
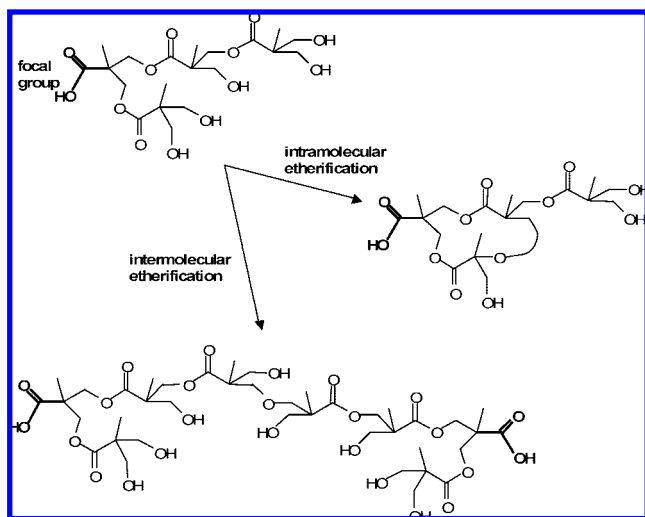
0.5 can be identified independent from the type of the reaction conditions. These results were confirmed later in our own work in which hb aliphatic–aromatic polyesters had been fractionated according to molar mass[486] and the individual molar mass fractions showed also an increase in the degree of branching in the oligomer molar mass region.

Effect of Side Reactions on the Degree of Branching. Side reactions are usually accompanying the polymerization of hb products. Beside the equal reactivity of the different functional groups (see sections 2.1.1 and 2.1.2), the low extent of these side reactions is crucial for achieving a statistical degree of branching. Products of these side reactions are mostly intramolecular ring formations or cross-linking when A reacts not selectively enough with B. The cyclization is the most investigated side-reaction in AB_x or $A_2 + B_y$ polymerization processes and is described in a number of publications.[68,171,282,453,455−458,283,459,460] Kricheldorf[87] carried out extensive investigations on these structures and developed a cyclization theory in order to explain the deviations of the hb structures from the cascade theory of Flory. Indeed, ring formation cannot be identified using the usual spectroscopic and chromatographic characterization methods for synthetic materials. A systematic analysis and combination of techniques has to be applied. MALDI-TOF-MS is a powerful technique giving information about different structural formations and repeating units in complex polymer systems. However, MALDI-TOF alone cannot account for the extent of the cycles in the sample and how they are distributed along the different polymerization degrees represented in the hb sample. A combination with NMR[88,283,459] measurements and sometimes even with SEC separation of the broadly distributed samples can lead to valuable information about distribution of intramolecular ring formation within the complex mixture of hyperbranched macromolecules.

Depending on the structure of the cycles formed, SEC-UV can be applied to indicate cyclization. In the work of

Scheme 47. Etherification as a Side-Reaction in an Aliphatic hb Polyester: Intramolecular Etherification Leads to Cycles, While Intermolecular Etherification Leads to Molecules with More than One Focal Unit[283]

Simon et al.,[458] the special UV absorbance of β-ketoester was used to indicate their formation. β-Ketoesters are the product of the backbiting reaction during self-condensing group transfer polymerization of methacrylate, leading to cycles that develop as the reaction proceeds and are especially present in the low molar mass region. However, quantitative analysis of the extent of cycles by this technique is not common.

Comprehensive investigation via MALDI-TOF-MS could lead to quantitative information about the cycle formation in hb molecules. An exact number of one cycle per 7 silicon atoms was determined in the work of Jaumann et al.[460] on polyalkoxysiloxanes.

The cyclization behavior of the Boltorn-type aliphatic polyester (AB_2 monomer **24**−**6**) has been discussed in a number of studies, e.g., applying polymer degradation techniques[15] or kinetic model calculations,[67] and a strong affinity to ring formation has been repeatedly confirmed.

The determination of cycles, i.e., *intra*molecular bonding, should be distinguished from the *inter*molecular side reaction with the same chemical character leading to a possible cross-linking. In the work of Komber et al.,[283] the etherification as a side-reaction during the polycondensation of 2,2-bis(methylol)propionic acid has been investigated. In this self-condensation, in addition to cycles from ether or ester intramolecular ring formations, cross-linking through ether formation between the molecules could also take place, leading to more than one focal group per molecule and, at very high polymerization degrees, to gelation (scheme 47).
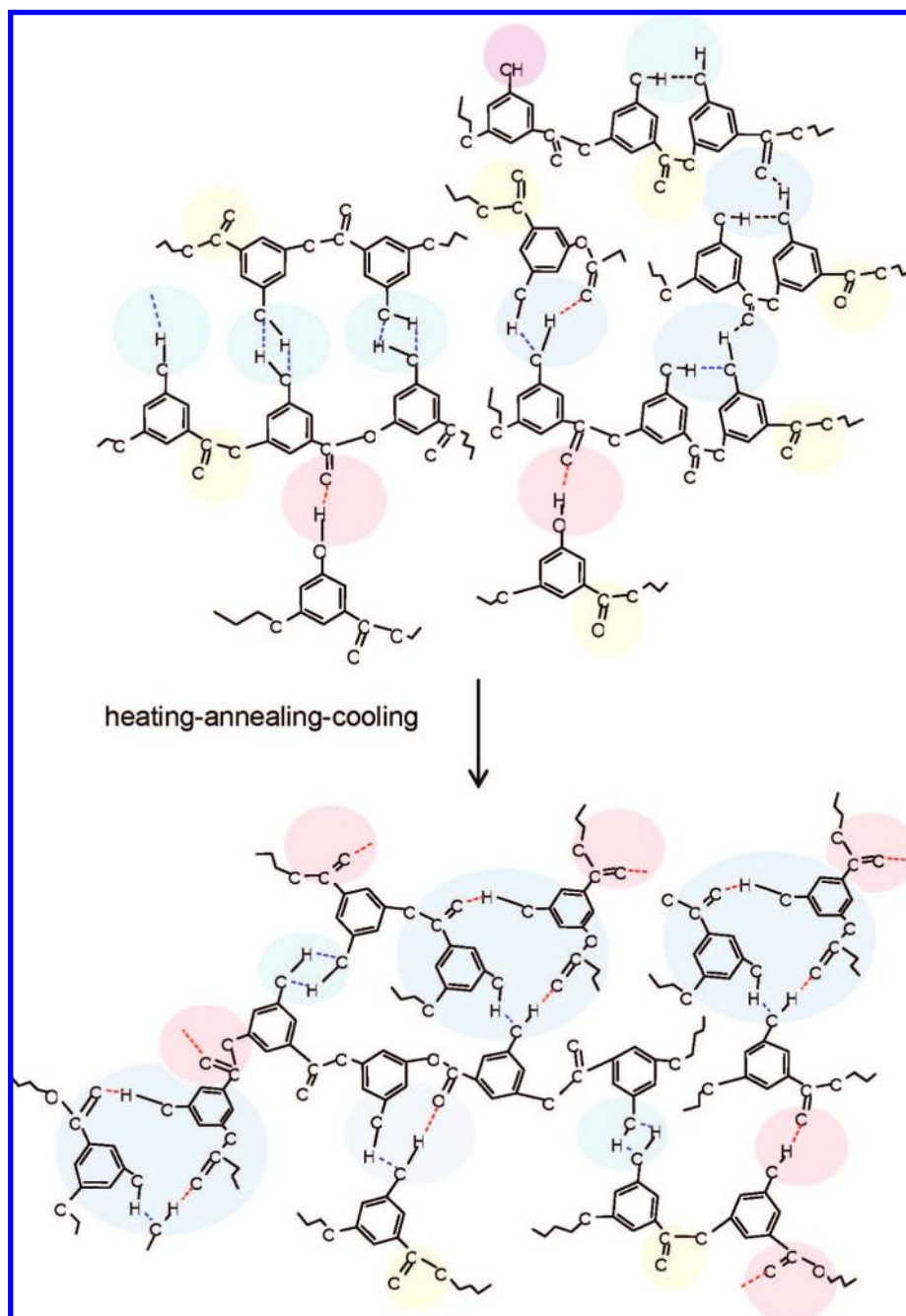
High-resolution ^{13}C NMR was used to identify the ether bonds in hb aliphatic polyesters. The amount of ether bonds was calculated after hydrolysis of the polyester. Independent from the catalyst that was used, up to 12% ether formation was found. These reactions take place obviously during the whole polymerization process and not only at high conversion of the A-groups. Further investigations on the polycondensation of the same monomer, with and without adding a core molecule, showed again a very high content, up to 50%, of ether formation, characterized by MALDI-TOF.[459] In this work, it was shown that the introduction of a core molecule led to some control over the etherification.

3.1.2. Intermolecular Hydrogen Bonding

Hydrogen bonding is a well-known phenomenon that plays a key role in biochemistry, defining the interactions of polar structures like proteins, nucleic acids, or polysaccharides. H-bonds have considerable importance in the area of synthetic polymers as well, since they can strongly influence solubility, crystallinity, rheology, blend formation, and, in general, processing of polymer mixtures. Because of the fact that hyperbranched polymers can possess a very large number of polar functional groups, they have a strong tendency to form H-bonds with neighboring molecules, solvent, water, or interactive surfaces. In the work of Schallausky et al.,[281] based on aliphatic−aromatic hb polyesters with phenolic end groups, a strong dependence of the glass transition temperature, T_g, was observed due to possible H-bond formation, which was dependent on the branching degree of the materials. Theoretically, the T_g should be reduced with increasing branching degree. However, the opposite effect was found in this work, i.e., increasing T_g with increasing degree of branching. The only possible explanation for this trend was the formation of an H-bond network, which becomes stronger with the increase in the number of phenolic end groups and the degree of branching, respectively. The development of the H-bond interaction in these polymers was investigated in detail by Mikhaylova et al.[461] using temperature-dependent Fourier transform infrared (FTIR) spectroscopy and curve fitting. In this work, heating−annealing−cooling cycles were applied to the polymer in the bulk and the changes in the H-bonding types were identified (scheme 48). The annealing was carried out at temperatures slightly higher than the T_g. Nevertheless, no influence of the changes in the H-bondings on the T_g was found, probably due to lower sensitivity of the thermal properties to this type of H-network formation. In the original, not annealed sample, a significant part of the hydroxyl groups interact via hydrogen bonds with each other or with ester groups including two or more participating functional groups in one H-bond complex. The increase of the mobility of the molecules due to heating above the T_g leads to weakening of the existing network of hydrogen bonds, followed by their rearrangement and creation of new H-bond complexes during cooling. It is worth mentioning that "free" OH groups were observed only during the annealing stage at 235 °C. Cooling of the system promotes the formation of new inter- and intramolecular hydrogen bonds; a thermally very stable H-bond network results.

The complete integration of the functional groups into H-bond complex formation is probably due to the fact that these polymers possess a sterically governed, very open and stiff structure (see section 3.2.2). This property enables the outer as well as the inner phenolic groups to form H-bonds; lower tendency for the formation of a complete H-bonding network was observed for aliphatic polyesters, which possess a more compact structure, hindering the interactions with the inner OH groups. This aliphatic polyester, a polycondensate of pseudo-4th generation from 2,2-bis(methylol)propionic acid with a core molecule, was investigated by Žagar and Grdadolnik.[462] They found strong interaction between OH and C=O groups with four different types of OH-group combinations. The authors made a comprehensive FTIR investigation including hydration and H/D exchange experiments. They concluded that there was a very strong, thermally controllable H-bonding network reorganization and found that a number of OH and C=O groups are not

Scheme 48. Reorganization of H-bonds after Heating and Annealing of the Aromatic hb Polyester above T_g (227 °C) and Subsequent Cooling; Types of the H-bond-Complexes Are Indicated by Different Colors[461]

heating-annealing-cooling

participating in this network, probably due to the very compact globular structure of the aliphatic hb molecule.

Thus, hydrogen bond formation in hb polymers with polar end groups strongly influences properties like solubility, glass transition temperature, and, of course, melt rheology. From the practical point of view, one should also notice that an often observed strongly reduced solubility in hb polyesters or polyamides after heating (drying) might be the result of the formation of a strong hydrogen bond network and not necessarily that of the formation of a chemical network.

3.2. Solution Characterization

3.2.1. Molar Mass and Molar Mass Distributions

Because of the statistically driven polymerization process, hyperbranched polymer systems based on AB_x monomers exhibit very broad molar mass distributions. These distributions broaden with the degree of polymerization, which can be explained by the higher probability for larger molecules to react with the monomer since they have a higher number of reactive groups. And indeed, if linear polycondensates theoretically reach a polydispersity of not more than $M_w/M_n = 2$, molar mass distribution of statistically hyperbranched samples is directly dependent on the degree of polymerization (DP) as $M_w/M_n \approx DP/2$.[25,77] Similar dependencies of the molar mass distribution on DP are derived from theoretical studies on hyperbranched polymers obtained by SCVP[106] with $M_w/M_n \approx DP$. The broad molar mass distribution can be influenced by the different reactivity of the functional groups of the monomers, using the method of slow monomer addition[73,74,463,464] or adding a multifunctional core molecule.[119,463] In $A_2 + B_3$ systems, the development of the molar
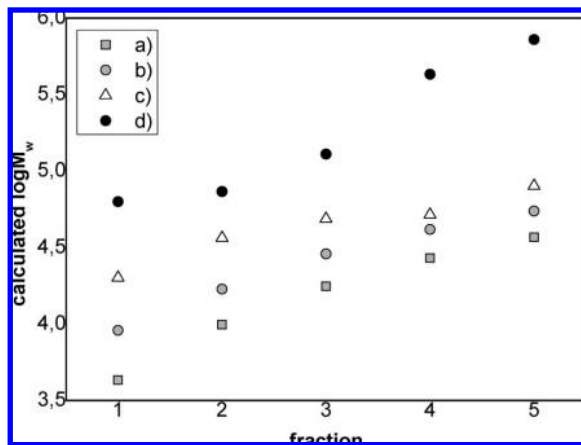
Figure 4. Deviation of the molar mass values for hb poly(ethera-mide) determined by different SEC-interpretation methods: (a) SEC-DRI detection and polyethyleneoxide standard; (b) SEC-DRI detection and polystyrene standard; (c) offline SEC-viscosity detection and universal calibration; (d) SEC-MALLS (static light-scattering detection).[467]

mass and molar mass distribution differs significantly from that of AB_x systems following gelation theories.[77,127,128,465] Thus, occurrence of gelation, polydispersity, and development of the molar mass are very sensitive to the functionality conversion, the ratio A/B, the amount of the added A_2 monomer, and the formation of cycles.[453,465] In the work of Unal and Long[297] on cyclization-free poly(ether ester)s, an additional rapid increase of the polydispersity after 75% conversion of A-groups has been observed.

Discussing molar masses and molar mass distributions for hb polymers, first one has to note that the determination of the absolute molar mass of hyperbranched polymers is not a trivial task. Because of their densely branched structure, their overall molecular density is increased compared to their linear analogues in a good solvent, and the well-known method for the determination of the full molar mass distribution of polymers, size-exclusion chromatography (SEC) with differential refractive index detection (DRI) or UV-detection and subsequent calibration with a linear polymer standard, can lead to strong deviations from the actual values of molar mass. A comprehensive comparison between different interpretations of the SEC chromatograms of hyperbranched poly(etheramide) using polystyrene and poly(ethylene oxide) as a calibration standard, as well as the method of the universal calibration,[466] has been carried out in order to find the best adequate method for processing the SEC results.[467] The comparison was made on the basis of the molar masses obtained by SEC coupled to DRI and static light-scattering detector (MALLS, multi-angle laser light scattering), the combination of which is known to give absolute molar mass values also for complex macromolecular architectures. The deviations between the values obtained by these three methods are extremely high, as shown in Figure 4. Even the data of universal calibration did not get close to the real molar mass values, although the intrinsic viscosity is incorporated into this calculation, taking into account the influence of the molecular density, according to the Flory−Fox eq 8, as explained below. This behavior was found to be typical not only for hyperbranched poly(ethera-mide)s but also for 100% branched poly(etheramide) den-drimers.[468] Because of the theoretical molar mass values lower than 5 000 g/mol, these dendritic molecules were successfully characterized by MALDI-TOF-MS.

However, at this point, we have to critically consider the benefits and limits of both, mostly applied absolute methods for molar mass characterization in dendritic systems, static light scattering and MALDI-TOF. Static light scattering alone leads to reliable information about the weight-average molar mass of hb polymers, in the case that no aggregates are formed in the solution.[469] However, this information is not enough with respect to the broad polydispersities of hb polymers. In order to achieve complete information about the molar mass distribution of a hb polymer sample, the combination of SEC-DRI-MALLS is essential. According to eq 7,

$$R_\theta = \frac{4\pi^2 n_0^2 \left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)^2}{\lambda_0^4 N_L} cM \tag{7}$$

the determination by MALLS of the lower molar mass region requires high contrast of the polymer solution to the solvent, i.e., a high refractive index increment, $\mathrm{d}n/\mathrm{d}c$, or high concentration, but the concentration used in SEC is limited. Even if these conditions are fulfilled, reliable MALLS molar mass determination is restricted to the high molar mass area. In order to overcome these problems, special interpretation methods could be applied for complete analysis of the molar masses.[470]

MALDI-TOF-MS is a powerful method for detection of molar masses of monodisperse samples. A limitation is due to the fact that, in broadly distributed samples, the lower molar mass species are preferably activated for desorption and, hence, the higher molar masses are not detectable or their intensity is so low that they are ignored. Therefore information about the complete polydispersity of the hb sample cannot be achieved. In order to apply this method for hb polymers, it is again reasonable first to separate the polymer in nearly monodisperse fractions and afterward to measure them using MALDI-TOF-MS.[459,460,471,472] Beautiful work has been done using the hyphenation of SEC with MALDI-TOF-MS. Jaumann et al.[460] achieved complete characterization of hb polyalkoxysiloxanes by this combination method, reaching molar mass values of more than 10^6 g/mol in the narrow distributed fractions. Montaudo[471] also treated the topic of MALDI-TOF-MS of hyperbranched polyesters exhaustively in his work. An additional advantage of MALDI-TOF-MS is the access to information about specific structural properties. Nevertheless, this technique is limited not only to samples or fractions with low polydis-persities but also in general to low molar mass polymers, which can be successfully detected quantitatively. For the purpose of analyzing high molar mass hb polymers, MALLS is definitely the better choice.

The usual way to conduct separation of polymers, SEC, is based on the well-balanced interactions between column material, solvent, and sample. In order to achieve complete separation according to size and to determine reliable polydispersity values, interactions between sample and column material have to be excluded. This is not always possible in the case of hb polymers. As multifunctional materials, interactions with column material are guaranteed. It has been repeatedly observed that this problem is exacerbated for higher molar mass products. The explanation for this phenomenon cannot simply be that the absolute number of end groups per macromolecule increases with the molar mass since the molar amount of end groups in the sample keeps constant. The most reasonable explanation is
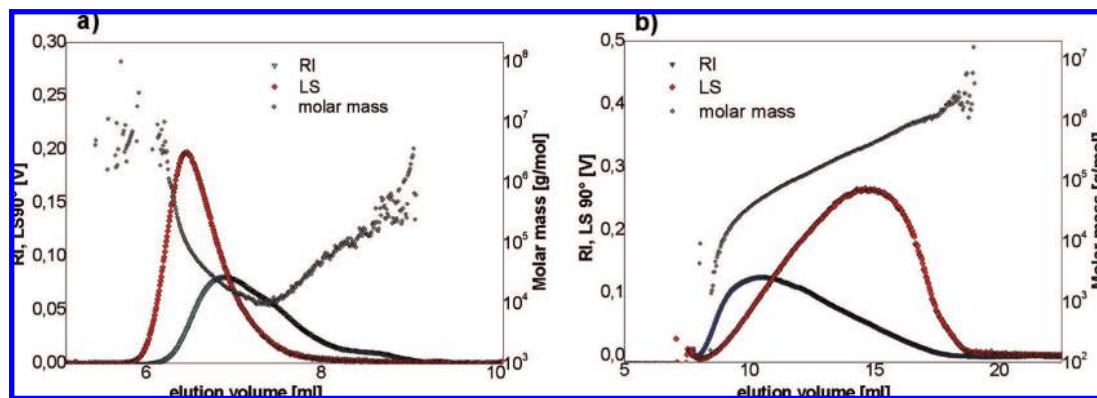
Figure 5. Separation of aromatic hb polyester by SEC-MALLS and A4F-MALLS: (a) SEC separation of sample with M_w = 40 000 g/mol does not take place according to size due to strong interactions with column material; (b) A4F separates sample with M_w = 161 000 g/mol according to the molar mass.[470]

an interplay between end group interactions and the change in molecular shape with molar mass as discussed in the next section. Several methods are employed to reduce these troublesome interactions, e.g., changing the solvent or the column material, or adding salts to the eluent.[467,469] However, these actions are often ineffective when it comes to multi-functional materials. A solution has been found for the separation of complex functional polymers using a column-free method—the asymmetric flow field flow fractionation (A4F). This recently commercialized technique separates the molecules according to their size in a channel with a membrane using the forces of an eluent cross-flow.[473,474] Interactions with the channel material (regenerated cellulose) do not affect the analysis, and the only limitation is coming from the membrane, which is porous for molecules with molar mass lower than ~5 000 g/mol. Therefore, this low molar mass region is not analyzed. Figure 5 shows a comparison between SEC-MALLS and A4F-MALLS measurement on an aromatic polyester with a high number of phenolic groups. The dependence of the molar mass from the elution volume shows clearly that the SEC column is not completely separating the polymer according to molar mass even for low molar mass samples (M_w = 40 000 g/mol), but that there are additional interactions disturbing this process. SEC separation is not effective at all for higher molar masses (M_w = 161 000 g/mol) due to very strong interactions with the column material. However, a linear molar mass/elution volume dependence can be observed after A4F separation, where the lower molar mass species elute first followed by the higher molar masses.

3.2.2. Molar Mass Dependencies of Structure Parameters

From the molar mass dependences of intrinsic viscosity [η], radius of gyration R_g, and hydrodynamic radius or second virial A_2 coefficient, conclusions about the molecular shape, density, and self-similarity can be obtained. These values are usually determined by viscosity measurements and scattering methods, whereas the effect of branching can strongly influence them. The solution behavior of linear polymers is well-described by quite general theories. The introduction of branches in a polymer structure, even if the branches are formed by linear segments, results basically in a different topology, which is not governed by the common universal laws. The situation moving from long to short chain and treelike branches, as in the case of hyperbranched topologies, is even more complicated. The solution theory of the intrinsic

viscosity of branched polymers is based on the Flory–Fox equation:

$$[\eta] = \Phi\left(\frac{R_g^3}{M}\right) \tag{8}$$

This relationship can easily be applied for linear polymers due to the fact that the draining factor Φ asymptotically becomes a constant, i.e., is not dependent on the size of the molecules.[475,476] In the case of branched polymers, an increasing segment density leads to an increase of the draining parameter,[127,477] which is contradicting the universality of this relationship. Indeed, comprehensive investigations on fractionated hyperbranched samples of poly(etheramide)s showed for the first time experimentally that the Kuhn–Mark–Houwink–Sakurada (KMHS) dependence of the intrinsic viscosity on the molar mass (eq 9) is not constantly increasing as observed for linear and star or long-chain branched polymers:

$$[\eta] = K_\eta M^\alpha \tag{9}$$

Typically, the KMHS exponent α is a quantity for the shape and compactness of a polymer in a certain solvent. There are many investigations on this parameter, and usually values of $0.3 < \alpha < 0.5$ for hb polymers were found,[32] whereas for a linear statistical coil in a good solvent, values of $0.5 < \alpha < 1$ are typical. Most of the studied hb polymer systems were investigated with regard to their KMHS exponent by an online coupling of SEC with a viscosity detector, leading to approximately linear dependencies, as shown in Figure 6.[32,63] Surprisingly, simulation on this behavior showed that, as for dendrimers,[478,479] the KMHS relationship should change exponentially for a statistical dendritic branching.[480–482] The first experimental results, which supported these theoretical calculations, were obtained after elution fractionation of the hb poly(etheramide)s leading to narrow molar mass fractions with a very broad range of molar masses of samples having the same chemistry, DB, and branching topology (figure 6). As theoretically expected, the maximum in viscosity was achieved above molar masses of 100 000 g/mol, and subsequently, the open dendritic molecular structure ($\alpha = 1.5$) becomes more dense at the higher molar masses ($\alpha = 0.1$).

The behavior of the hb poly(etheramide) shown in Figure 6b resembles strongly the results of several simulation studies on intrinsic viscosity behavior of dendritic molecules with
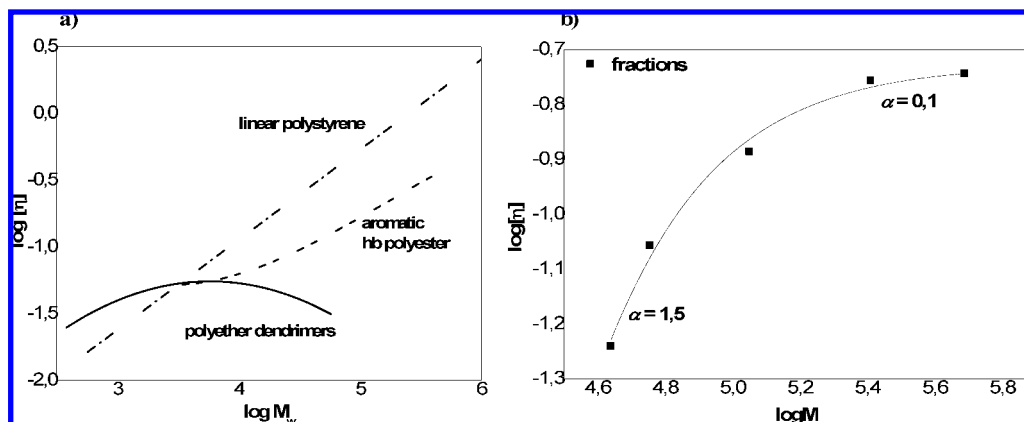
Figure 6. KMHS plots: (a) linear polystyrene and aromatic hb polyester[63] and polyether dendrimers[478] measured by online SEC-viscosity detection and (b) fractions of hb poly(etheramide) measured offline by SEC-MALLS and viscometer.[467] Adapted with permission from ref 467. Copyright 2002 Elsevier.

defined DB and polymerization degree. For these simulations, different procedures were used: kinetic bead-rod model was used in the calculations of Aerts[480] and Lescanes and Muthukumar;[481] Brownian dynamics including hydrodynamic interactions and calculations on the excluded volume were carried out by Lyulin et al.;[483] and Widman and Davies used resonance ionization spectrometry (RIS) metropolis Monte Carlo simulations.[482] Independent of the calculation procedure, the authors found a clearly visible but disappearing dendrimer-like maximum with decreasing DB from 1.0 to 0. However, in these studies, the influence of the branching distribution and polydispersity in actual samples were not taken into account. With the introduction of the Wiener Index[484] in the work of Sheridan et al.,[485] the first steps were made in the direction of simulating actual, nonmonodisperse hyperbranched systems. Further studies on the complex influence of multidimensional polydispersity (DB, molar mass, and Wiener index) perhaps will give an answer to why online SEC−viscosity measurements do not reflect the simulated KMHS behavior. Obviously, this observation has to be a result of simultaneous elution of molecules with similar hydrodynamic radius but different degree of branching, i.e., DB distribution in one fraction.

However, even using elution fractionation in order to achieve low polydispersities at different molar masses and to extract the KMHS behavior for a certain hb sample, we certainly cannot always obtain the predicted relationship as expected from theoretical studies. This was observed for a hb aromatic−aliphatic polyester, synthesized from the AB_2 monomer 4,4-bis(4-hydroxyphenyl) valeric acid (**24−4**). In this case, a very open molecular structure in solution was obtained with α = 0.75.[486] At the same time, an aliphatic hb polyester from the AB_2 monomer 2,2-bis(hydroxymethyl)propionic acid (**24−6**) changes its shape from open to dense (α = 0.7 to α = 0.1), exactly as theoretically predicted in the region of 100 000 g/mol (Figure 7).[487] In order to exclude the influence of the polar functionalities on the solution behavior, the polar end groups of both polymers were 100% modified by nonpolar end groups.

Molecular dynamic (MD) simulations of both types of hb molecules shed light on this question. A comparison of the shape of both molecules without further interactions and interacting with a good solvent can be seen in Figure 8.

Different compactness of the molecules without solvent interactions can clearly be seen in the aromatic and in the aliphatic molecules. On the one hand, this is an effect of
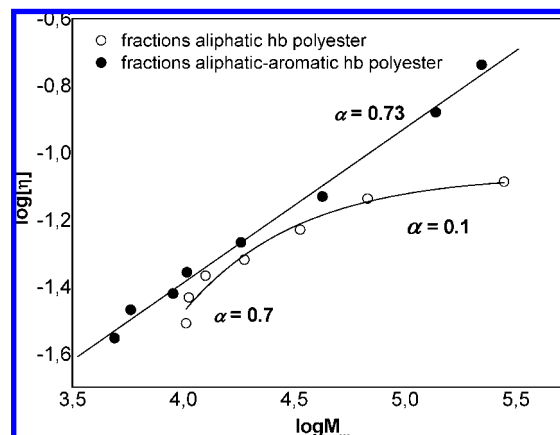

Figure 7. KMHS plot of aliphatic[487] and aliphatic−aromatic polyester[486] with nonpolar end groups.

the size of the monomers defining the distance between the branching points; on the other hand, the rather stiff structure and steric hindrance do not allow the aliphatic−aromatic macromolecule to take a more compact shape. Interactions with a good solvent do not further influence the rather open structure even at higher molar masses. The opposite case was observed for the aliphatic polyester: interactions with a good solvent are leading to a more open molecular structure compared to the model in the solvent-free state as an effect of better flexibility, even though in total the branching point distance is much shorter and the macromolecules appear more compact. Hence, changes in molar mass may change the shape in solution of these hb polyesters, leading to the well-described maximum in the KMHS plot. In other words, the chemical character of the polymer units, as well as end groups, indeed plays an important role in the solution properties of the hyperbranched polymers and cannot be excluded when searching for explanations for their unusual solution behavior.

Unfortunately, up to now, there are still no complete investigations using preparative elution fractionation on hb polymers having a broad variation in the degree of branching, due to the required very time-consuming and costly experimental work. For this reason, only results obtained from SEC−viscosity−MALLS measurements are available, which are significantly easier to obtain, but this method combination so far leads to linear KMHS plots[32,281] that are not consistent with the theoretical predictions described above.
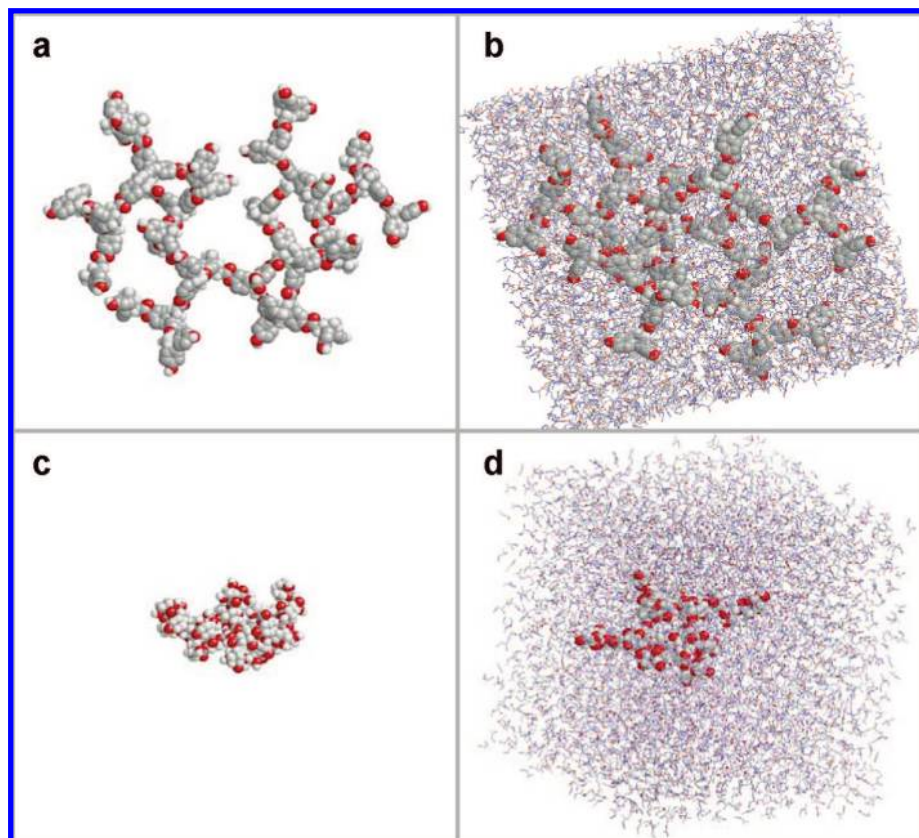
Figure 8. Molecular dynamic simulation of hb polyesters with 35 monomer units at 300 K: (a) aliphatic−aromatic hb polyester; (b) aliphatic−aromatic hb polyester interacting with solvent N,N-dimethylacetamide; (c) aliphatic hb polyester; (d) aliphatic hb polyester interacting with solvent N,N-dimethylacetamide.[486]

In most of the cases, dilution of the branching degree with a bifunctional monomer is leading to an increase of the KMHS exponent α, as expected for increasing linearity of the structures. Again, the influence of the chemical structure cannot be excluded. A well-balanced combination of monomers is essential in order to obtain a clear dilution of the branches without further side effects, changing the overall properties of these systems. An extreme example is the gradually branched analogues of the hb aliphatic−aromatic polyester described above. Dilution of the branches using copolycondensation of AB_2 and AB monomers (3-(4-hydroxyphenyl)propionic acid) led to a clear dependence of the DB on the monomer ratio (Figure 3). Online SEC measurements of the KMHS behavior, however, led to a decrease in the KMHS exponent at lower DB (figure 9). Another way for dilution of the branches in this polymer is using the monoprotected $AB_{2,mp}$ monomer and subsequent deprotection of the polymer, leading to homopolymer of reduced DB. In this case, the expected increase of α was experimentally observed. Obviously, in the first case, because of the very stiff structure of the AB_2 monomers, their combination with more flexible AB monomers enables the polymer molecules to take a sterically favorable conformation by becoming more compact. In the case where monoprotected $AB_{2,mp}$ monomer for branching dilution was used, no additional flexibility was permitted, leading to higher compactness and, hence, higher α values, typical for statistical linear coils in a good solvent. At this point, it should be mentioned again that the measuring of the KMHS dependence was carried out using an online SEC−viscosity detector, which is not ideal with respect to a clear distinction between multiple polydispersities. For this

Figure 9. KMHS exponent dependence on the degree of branching for two types of aliphatic−aromatic copolyesters: synthesized by copolycondensation of $AB_2 + AB$ monomers[486] and by copolycondensation of AB_2 monomer with the monoprotected $AB_{2,mp}$ and subsequent deprotection.[488]

reason, deviations from the values obtained after elution fractionation might be observed.

Similar to the KMHS relationship, a relationship for the dependence of the radius of gyration on the molar mass exists as

$$R_g = KM^\nu \qquad (10)$$

As branching reduces viscosity, it is also reducing the volume of the molecule at a given molar mass, due to

increasing density. This property of branched molecules is used for their characterization, and for instance, in long-chain branched polymers, it enables even the calculation of the branches per molecule on the basis of the universal law (eq 8), described above. Hyperbranched polymers show even a stronger shrinking effect than long-chain branched polymers relative to their linear counterparts,[489] described by the contraction factors g and g':[490,491]

$$g = \frac{R^2_{g,\text{branched}}}{R^2_{g,\text{linear}}} \tag{11}$$

$$g' = \frac{[\eta]_{\text{branched}}}{[\eta]_{\text{linear}}} \tag{12}$$

Theoretical as well as experimental investigations have been carried out in order to obtain a quantitative relationship between both contraction factors:

$$g' \approx g^b \tag{13}$$

Stockmeyer predicted theoretically $b = 1.5$ for branched polymers according to the universal law.[491] Zimm[492] found that, for certain branching topologies, b should be 0.5. Empirically there were different values found for this parameter, lying between 0.5 and 1.5 for long-chain branched and star polymers. For hyperbranched polymers, however, b is strongly deviating from this regime. Values of $b > 2$ for glycogen[493] and $b = 0.71$ for dextran[494] have been found, whereas for hb polyesters $b = 0.26$ was calculated.[495] These strong deviations can be explained only by the nonconstant draining factor for branched polymers, with strong dependence on g[495,496] due to varying compactness and interaction with the solvent, respectively.

Commonly, information about the molecular dimensions of dissolved polymers leads to the exponent ν from eq 10. This exponent can be easily transformed in a value describing the fractal dimensions $d_f = 1/\nu$ of the polymer molecules. In most of the cases, where the fractality of the hb polymers has been investigated, values between 2 and 3 are reported, which means fractal dimensions between a disk and a hard sphere were found. For perfect dendrimers, these values are approaching 3, and for linear polymers, they are in the range of 1.66 and 2. The fractal dimension for hb polyesters was calculated to be 2.38,[495] and similar results were found for dextrane and starch by the group of Burchard.[497,498]

There are a couple of parameters, describing branching similar to α and ν, that are extracted from measurements of thermodynamic, hydrodynamic, and viscosity radius by static or dynamic light-scattering and viscosity measurements, respectively.[493,495,499,497,500,501] But probably one of the most sensitive parameters to branching topology is that coupled to the coil–coil interpenetration function Ψ, which describes the ability of polymer molecules to interact with each other:[127]

$$A_2 = 4\pi^{3/2} N_A \left(\frac{R^3_g}{M^2} \right) \Psi \tag{14}$$

Combining eq 14 with the Flory–Fox eq 8, we will obtain

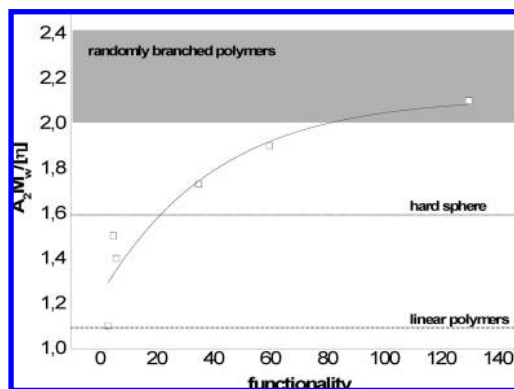$$\frac{A_2 M_w}{[\eta]} = \frac{\pi^{1/2} 6 \Psi}{5 \Phi} \tag{15}$$

Figure 10. Dependence of $(A_2 M_w)/([\eta])$ on the functionality for star and randomly branched (hyperbranched) polymers at high molar masses adapted from Burchard[127] and Galinsky.[502] Dotted lines are theoretical values for linear polymer and hard sphere; the gray area corresponds to values for randomly branched and hyperbranched polymers.

For linear polymers, the value of $(A_2 M_w)/([\eta])$ is approximately 1.07, and for hard spheres, it should be 1.6. With increasing branching density, this value should increase because the interpenetration ability of the molecules is decreasing more rapidly than the draining of the solvent into the polymer coil, i.e., Ψ is increasing faster than Φ and $(A_2 M_w)/([\eta])$ is increasing, respectively. This behavior has been observed for stars[127,392] and was expanded to random starch polymers in the work of Galinsky and Burchard,[502] as described in Figure 10.

For randomly branched and hyperbranched polymers, the authors predict values of more than 2, which was supported by scattering results of dextran[497] and hyperbranched polyesters.[495] Interestingly, it was shown that this value is getting larger with increasing molar mass, reaching a maximum at approximately 100 000 g/mol, a value which could be correlated with the theoretically predicted maximum in the KMHS behavior (see above).[480,482,485]

Regarding the solution properties of hyperbranched polymers, new and interesting relationships have been observed. However, a generalized theory on these structures is not yet developed and remains a significant challenge, not only due to the branched architecture and the variations in the backbone structure but also due to the significant influence of the very high number of end groups on the solution properties.

3.3. Bulk Characterization

3.3.1. Thermal Properties

The thermal properties of polymers like melting point and glass-transition temperature are strongly influenced by branching. Usually branching reduces the crystallization ability, and the branching topology and length significantly determine the extent of this effect. Hyperbranched polymers are usually formed by very short and dense branches, which completely prevent crystallization. There are only a couple of examples where crystallization has been observed either due to modification with long chains[503] or due to branching dilution,[281] where the length of the linear parts is sufficient for formation of crystalline domains and a very broad melting peak can be observed after characterization with differential scanning calorimetry. Another exception is the tendency of some hb polymers to assemble into liquid crystalline structures.[351]
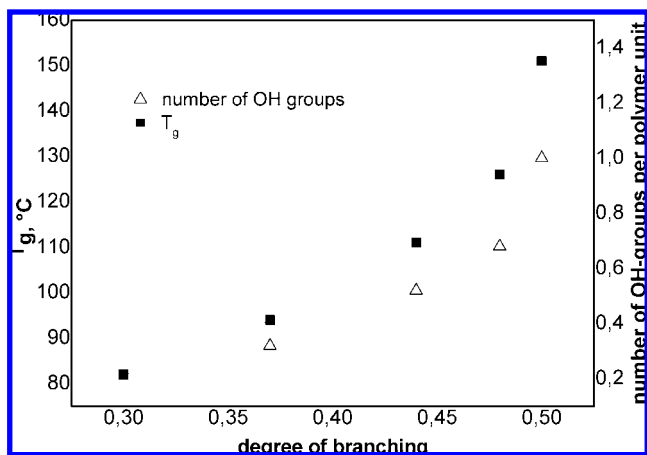
Figure 11. Dependence of T_g and number of OH groups on the degree of branching for an $AB_2 + AB$ polyester with varying content of AB comonomer.[281]

Glass-transition temperature (T_g) depends on the mobility of the polymer backbone, which in turn is sterically or chemically defined. In addition, the free volume of the molecules, which is reflected by the T_g, depends on the end group interactions. From the topological point of view, T_g is decreasing with branching degree and branching density, due to limitations in the molecular mobility. Such behavior has been observed in hb polyetherimides,[504] where mobility of the molecules is directly coupled to the DB. Nevertheless, direct comparison of linear, hyperbranched, and dendritic aromatic polyesters having identical repeating unit chemistry and number and nature of functional groups showed practically identical glass-transition temperatures.[505] On the other hand, random copolymerization of two different AB_2 monomers leading to pure hb structures were compared to linear random copolymers of similar chemical character and showed identical tendencies of T_g in complete agreement with the Fox equation.[506] This fact shows that the chemical character of the backbone is the primary consideration for T_g, and the branching topology plays a secondary role.[507]

The end group effect on T_g in hb systems is very strong as well. In cases where the increasing number of polar end groups can lead to strong interactions between the molecules with increasing DB, the opposite behavior has been observed as in the case of gradually branched polyesters by copolymerization of AB_2 and AB monomers (Figure 11). For this type of polymer, H-bonding interactions have been confirmed by FTIR measurements (see section 3.1.2), and these strongly increase with increasing DB and end group number. Amplification of the H-bonds effect on T_g could stem from the increasing flexibility of the backbone at higher contents of AB units in the polymer structure (Figure 11).

Longer linear parts in hb polymers are suspected to play the role of a plasticizer, as shown in the work of Schmaljohann et al.[503] The authors modified the end groups of hb aromatic polyesters that exhibited a starting T_g of 220 °C. The modification of the phenolic end groups of this polyester was accomplished by adding linear alkyl chains with varying chain lengths up to 14 C-atoms. This modification led to a strong decrease of T_g (−50 °C) and an additional melting peak at an alkyl chain length at 14 C-atoms.

In summary, the effect of the dendritic branching on the glass transition cannot be explained simply by the particular branching topology, but it is defined by the combination of the monomer chemical character and the number and type

of functional groups in the polymer and depends certainly on the combination of linear and branched units in one macromolecule.

3.3.2. Melt Rheology

One of the major advantages of hyperbranched polymers is their rheological behavior in the melt, which differs strongly from that of linear polymers and is extremely useful in applications, e.g., modifying the processing properties of linear polymers.[13] In order to take advantage of hb polymers for these applications, fundamental knowledge about the effect of the architecture on the rheological and processing properties is needed. And indeed, a number of experimental rheology investigations on hyperbranched polymers have been carried out showing strong deviations[448,508−510] from the theories developed for linear and star or H-shaped polymers, which have been the subject of theoretical and experimental investigations for several decades.[511−516] These deviations can be explained by the very high DB and the dense branching topology, which make it difficult for the hb molecules to entangle. For this reason, hb polymers should exhibit the properties of unentangled macromolecules,[517,518] reflecting the behavior of Newtonian fluids, where the degree of branching, topology, and especially end groups have a strong influence on the rheology.

Efforts have been made to produce hb polymers with defined variations in the branching degree of the same chemical composition, where the influence of end groups is excluded.[309,519−521] The simplest example of such polymers are polyethylenes, which were presented in the work of Ye et al.[522,523] A comparison between polyethylene with different branching topologies—from dendritic to nearly linear—was made using dynamic oscillation and steady shear measurements. In the case of highly branched polymers, Newtonian flow behavior has been observed in contrast to the typical shear thinning for the polymers with nearly linear structure. The stress relaxation expressed by the storage (G') and the loss moduli (G'') was investigated, leading to similar dependencies in the low-frequency region according to the dynamic scaling theory based on the Rouse model.[524] However, differences were observed at higher frequencies, where an elastic rubber plateau was observed in the case of the less-branched polymers, typical for polymer chain entanglements (Figure 12).

A similar behavior for linear and branched poly(methyl methacrylate)s was observed from Pakula et al.[520] Detailed interpretation of these results as well as additional rheological investigations on highly branched polystyrenes and hyperbranched polyesters[509,510,525] led to the conclusion that macromolecules with high branching density behave like polymers and soft-colloids simultaneously and exhibit strongly limited inter- and intramolecular entanglement.

Recent investigations on dendronized poly(norbornene) showed a clear dependence of the complex modulus on the degree of polymerization and on the size of the pendant dendrons. G' was affected by the dendron generation at lower DP, which is getting similar at higher DP.[526]

Besides the branching density, the influence of the end groups on the chain mobility in hb polymers and on their rheology is of great importance.[503,525] One example is again hyperbranched poly(etheramide),[527] which originally possesses a high number of OH end groups and exhibits elastic behavior with high viscosity at low frequencies. After acetylation of the end groups, strong reduction of the
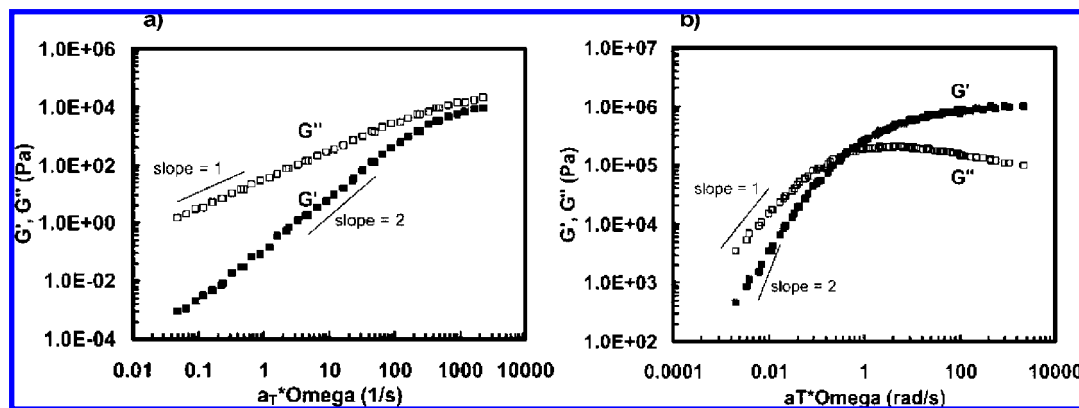
Figure 12. Storage modulus G' and loss modulus G'' vs angular frequency at 60 °C for polyethylene with (a) highly branched topology and (b) nearly linear chain topology. Reproduced with permission from ref 523. Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA.
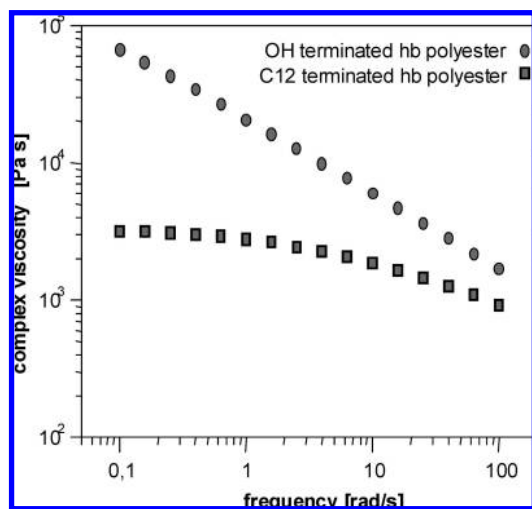

Figure 13. Complex viscosity versus frequency for OH- and C12-terminated aromatic hb polyester.[503]

complex viscosity can be achieved due to the mitigation of interactions between the polar functionalities. The introduction of these polymers, with OH as well as with acetate end groups, in very small amounts (0.1%) into a linear polyamide matrix led to a significant reduction of the complex viscosity of the linear polymer. A further very strong reduction of the complex viscosity of these blends was obtained after modification of the poly(etheramide) with alkyl chains; however, this effect was accompanied by phase separation of the blend components. The phase-separation problem has been solved by inserting oxazinone end groups into the hb polymer, which in turn led to a strong increase of the viscosity due to reactive blending with the linear polyamide.[528]

The rheological properties of hyperbranched aromatic polyesters before and after modification with alkyl chains showed again strong effect of the end groups on the rheology of these polymers.[503] Figure 13 shows the complex viscosity dependence on the frequency for both polymers.

For the OH-terminated polymer, nonentangled elastic behavior can be observed, while typical behavior for a viscous melt with a plateau at low frequencies after 100% modification of the end groups with C12 alkyl chains was found. These results are supported by the analysis of the complex modulus of both polymers. G' and G'' for the OH-terminated polyester are completely identical even in the low-frequency region, showing equal viscous and elastic com-

ponents. For C12-modified hb polymer, a strong reduction of both moduli has been observed and the relation between them corresponds to an increased viscous behavior.

The effect of end groups is also related to the above-discussed tendency for formation of hydrogen bonds, which has been investigated in the work of McKee et al.[521] The authors compared linear and randomly branched poly(alkyl methacrylates) systematically modified with end groups leading to quadruple H-bond interactions. Storage modulus as well as dynamic viscosity master curves and the development of the relative zero shear viscosity show that the H-bonding between the end groups dominates the melt rheological response and is independent of the existence of branching even at small modification degrees. Differences between both linear and branched polymers are visible only for the nonmodified polymers.

3.3.3. Thin-Film Properties

The investigation of dendritic polymers in thin films was motivated by the potential use of hb polymers in various thin film applications. Thus, the strong sensitivity of hb films toward humidity and volatile organic compounds might open an application of these materials as chemical sensors.[529−531] The potential to fine-tune protein interactions with thin films of hb polymers opens applications in diagnostics and multifunctional coatings.[532−536]

In a thin film, the large number of functional groups of the hb polymers dominate surface properties and enables specific interactions with analyte molecules and biomolecules. In order to control the properties of hb thin films, an understanding of the influence of branching topology, polymer flexibility, polymer backbone, and type of the end groups on surface properties is needed, and the confinement effect of the thin film geometry on these properties has to be clarified. Such systematic and detailed investigation has been carried out on hb polyesters. The thin films of these polymers, prepared by spin coating, are completely homogeneous with thickness of only a few molecular layers, proven by ellipsometry and AFM.[533] The influence of the polymer backbone on the density of these films is of immense importance.[307,537] A comparison between aliphatic, aromatic, and aliphatic−aromatic hb polyesters at the same conditions was carried out[537] (Scheme 49).

Direct dependence of the density of the films on the monomer structure and flexibility was found. This was calculated from the film thickness and refractive index

Scheme 49. Hyperbranched Polyesters with Different Backbones for Thin-Film Investigations; The Thin-Film Density at 50 nm Film Thickness Was Determined from the Refractive Index Measured by Ellipsometry[537]

detected by spectroscopic vis-ellipsometry. These results completely support the MD simulation results of the aromatic−aliphatic and aliphatic polyesters in dilute solution described in section 3.2.2. Interesting observations were made on the different swelling kinetics of the hb thin films in a buffer solution depending on the monomer geometry. Very fast swelling corresponded to a very flexible backbone and higher extent of free volume, whereas the swelling rate of the stiffer aromatic−aliphatic hb structures was lower. Additionally, the hydrophilicity increased with decreasing aromatic content and increasing flexibility of the molecules.

In addition to the type of backbone, another way of adjustment of the surface polarity is film annealing above the glass-transition temperature, giving the polymer molecules the possibility to undergo a favorable reorientation. This leads to reorganization of the polymer segments to form a stable H-bond network, as described in section 3.1.2, and a simultaneous decrease of the surface free energy of the film, indicated by dynamic contact angle measurements, was observed.[461,538]

The swelling properties as well as the sensitivity of the hb polymer films to analyte molecules can be strongly influenced by the type of the functional groups.[529,530,533,538,539] Comprehensive evaluations of thin-film properties of hb aromatic polyesters with hydroxyl (−OH), carboxylic (−COOH), and acetoxy (−OAc) end groups have been carried out using complementary spectroscopic methods, ellipsometry, contact angle measurements with axisymmetric drop-shape analysis, and electrokinetic measurements. Clear dependence of the film thickness on the air humidity and on the polarity of the end groups was found as depicted in Figure 14.

Similar results were found regarding the sensitivity of these hb films toward alcohols, and interestingly, the −OH

terminated sample could very sensitively distinguish between different freons measured by reflectometric interference spectroscopy.[530]

Obviously, this advantageous response of the hb thin films toward water, alcohols, volatile organic compounds, and biomolecules is strongly influenced by the type and number of the end groups and can be well-tuned by adjusting them. Indeed, a comparison of the OH-terminated hb polymers with nonpolar, modified hb polymers and linear analogous[537] shows clearly that the dominating feature in adsorption processes on thin films is not the branching topology but the large number of functional groups.

Besides the effect of backbone and end group type, the confinement in thin film geometries leads to special properties compared to a bulk. Using broadband dielectric spectroscopy, Serghei et al.[540] showed that hyperbranched polyesters in thin films exhibit pronounced deviations of their dynamic glass transition from a bulk behavior, which are stronger than observed for linear polymers, i.e., they take place at larger film thickness. This has to be attributed to their special branching topology, as suggested by Das et al.[541] on the basis of experiments and computer simulation of dendritic structures of different generations.

4. Summary and Perspectives

This review has covered the principle synthetic approaches toward hyperbranched polymers as well as various other highly branched polymer architectures developed over the last 20 years.

Initially discussed were hb polymers prepared by the classical AB_x approach as well as the broad variety of A_2+B_y combinations with the basic principles of the polymerization processes. Representative examples of the various polymer classes were presented including the advantages, disadvantages, and limitations of the various synthetic methodologies. A common feature for all these hb polymers is that they are prepared in an uncontrolled one-pot synthesis and have the potential of branching in each repeating unit. This review is certainly not exhaustive since it would not be practical to cover all examples, but the main material classes have been exemplified with selected representative structures.

The properties of hb polymers are unique when compared to any other branched polymer architectures due to the very dense branching. Characterization is a critical component of research in this area and this review focused on solution and bulk properties. The intention was to emphasize that this still
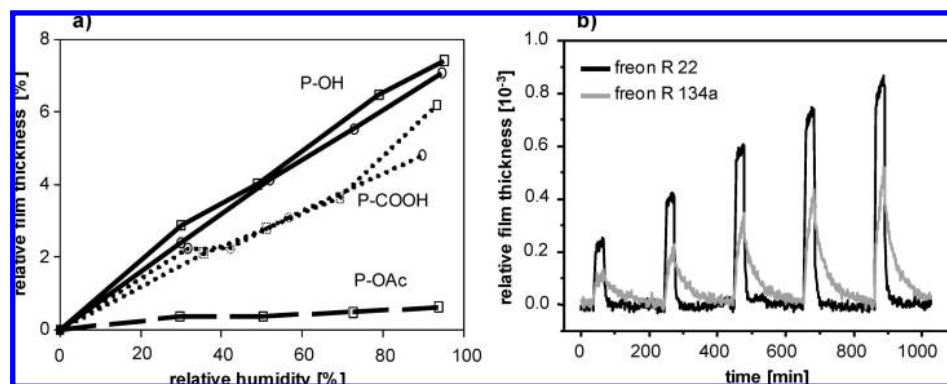

Figure 14. Film thickness dependence for thin films: (a) on the humidity for aromatic hb polyester with hydroxy, carboxylic (measurements on two different samples show high reproducibility), and acetoxy end groups[529] and (b) on the time and concentration of different types of freons for aromatic hb polyester with hydroxyl end groups.[530]

rather new polymer class cannot readily be characterized with the well-established methods, and thus, great care has to be taken to adapt characterization methods and to elucidate the structure before any structure−property relationships can be established. It is obvious that hyperbranched polymers are very complex structures with multidimensional, broad distributions, e.g., in molar mass, degree of branching, or chemical structure. They have a particular behavior in solution and in bulk that differs strongly from that of linear and star or less branched polymers; however, this behavior is not dominated solely by the branching, but the nature of end groups and the chemistry of the repeating units also play a significant role.

More recently, the field of hyperbranched or highly branched polymers has advanced not only by using various new reaction types like addition and cycloaddition processes, but also by including SCVP as well as ROMBP and the combination of different methodologies. In addition, the highly branched structures are increasingly combined with linear segments by various methods, e.g. through copolymerization or by addressing starlike architectures with hb cores as well as variations of arborescent type highly branched polymers. A major section of this review is thus dedicated to these methodologies, presenting again the basic principles as well as structural examples. The new chemistries and processes have broadened the structural varieties enormously, and still no end can be seen regarding new polymer architectures that will appear in the near future. These new approaches lead also to polymer structures of much higher molar mass and dimensions, to core−shell like structures, and the preparation of nano-objects and nanocapsules that show fully new property profiles.

The enormous progress in the synthesis and characterization on hb polymers has helped to close the property gap between these imperfect structures and perfectly branched dendrimers. Consequently, this has opened up potential application areas such as carrier molecules for therapeutics and self-assembled nanostructures for biomedical applications.

On the basis of the tremendous progress in this field, it is our strong opinion that highly branched polymer structures will play an even increasingly important role in the field of specially designed functional polymer materials and that new materials will enable many future high-tech and biomedical applications.

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