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The potential of cycloaddition reactions in the synthesis of dendritic polymers†

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Cycloaddition (CA) reactions have attracted recently strong interest not only for the preparation of linear polymers but also for the synthesis and modification of dendritic architectures. This review focuses mainly on the potential of various cycloaddition reactions in the field of dendrimers and especially hyperbranched polymers. The [4 + 2] Diels–Alder cycloaddition, [2 + 2 + 2] CA as well as 1,3-dipolar CA reactions including "click chemistry" will be addressed, and advantages of these reactions will be highlighted. High selectivity, thus high tolerance towards additional functionalities, high yields and often moderate to mild reaction conditions distinguish CA reactions from the often applied classical high-temperature polycondensation type reactions used mainly to synthesize hyperbranched polymers. Thus, besides the high potential in the synthesis and modification of perfectly branched dendrimers, cycloaddition reactions proved also very suited to prepare new types of hyperbranched structures.

Introduction

Dendritic polymers, the perfectly branched dendrimers as well as their hyperbranched cousins and a variety of combinations between dendritic and linear structures, are certainly among the most studied functional and specialty polymers today. Due to the highly branched, compact and highly functional structure with special reactivity, solubility and rheology features, applications in nanotechnology, biomedicine, sensors, and micro(nano)electronics, but also in a variety of reactive formulations are discussed. The reactions explored so far for the synthesis of dendritic polymers are numerous and are covered in a number of excellent reviews.[1–11] Nevertheless, to achieve high control of the structure and high yields in the polyreactions are still major issues which need to be addressed, and the lack of these are considered together with the restricted monomer availability and the high costs the limiting factors for the market introduction of dendritic polymers.

Cycloaddition (CA) reactions are known to exhibit the features needed urgently in dendrimer synthesis: they are very efficient and highly selective and allow even stereoselectivity! CA reactions have been used successfully in polymer synthesis already for 40 years,[12] an area reviewed excellently very recently by Goodall and Hayes[13] who also pointed out already the developments in dendrimer synthesis.

Therefore, one is not surprised that besides Michael *addition* reactions, which are used very successfully for the synthesis of polyamidoamine (PAMAM) and polypropyleneimine dendrimers,[1,2] special types of *cycloaddition* reactions have been also early on explored in the preparation of dendrimers.[14–16] Moving from addition to cycloaddition reactions offers even more control over the polyreaction with the potential to form fully new structural units and to achieve also stereo-control and even unusual effects regarding the degree of branching (DB) in hyperbranched products through the formation of special intermediate structures during the growth of the macromolecules. Even in the classical Michael addition reaction positive effects on the DB were observed. Hobson and Feast[17] reported poly(amido amine)s (PAMAM like) hyperbranched polymers using an amino-acrylamide AB_2 monomer. Unexpectedly, a degree of branching close to 100% was determined which could not be fully explained but it can be

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assumed that a special intermediate is formed during the reaction favoring the second branching.

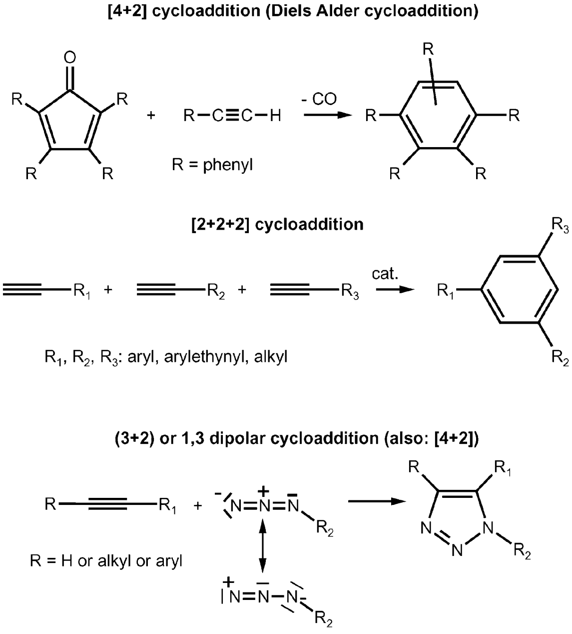
However, only recently, especially with further developments concerning the Huisgen 1,3-dipolar cycloaddition[18,19] towards the so-called "click chemistry",[20,21] the use of CA reactions has grown nearly exponentially, for both the preparation and functionalization of dendrimers and dendrimer–linear hybrids. In addition, CA reactions are also used very successfully in the preparation of hyperbranched polymers.

This perspective will thus point out these recent developments concerning the use of CA reactions for the synthesis and modification of dendrimers and especially hyperbranched polymers.

Cycloaddition reactions

Cycloaddition reactions[22] lead to the formation of new σ bonds *via* cyclic transition states which finally results in a cyclic product. In the intermediate state phase matched interactions between the highest occupied molecular orbital (HOMO) of one component and the lowest unoccupied molecular orbital (LUMO) of the other compound are involved which results in the formation of bonds in a concerted and thus highly controlled manner.[23] CA reactions are usually affected only to a very small extent by the medium used and they can be promoted by temperature or by light.[24]

The subclasses of these reactions are classified by the number of π electrons that are involved in the CA reaction *e.g.* [4 + 2] or [2 + 2]. The 1,3-dipolar CA also fits in this classification: it involves 6 π electrons and is denoted as [4π + 2π] (or [4 + 2]) type cycloaddition. However, it is often described as a (3 + 2) process to distinguish it from other [4 + 2] CAs which can cause some misunderstanding. Details on the mechanism and selection rules of the different CA reactions can not be given here and thus one has to refer to the literature.[18,19,25] However, it may be noted, that orbital symmetry controlled CA reactions will be antarafacial and suprafacial, according to the Woodward and Hoffmann selection rules, and this depends on the number of electrons involved as well as on the type of promotion (thermal or photochemical). In addition, other cycloadditions may occur which involve intermediate steps and which do not necessarily follow the Woodward–Hoffmann selection rules.

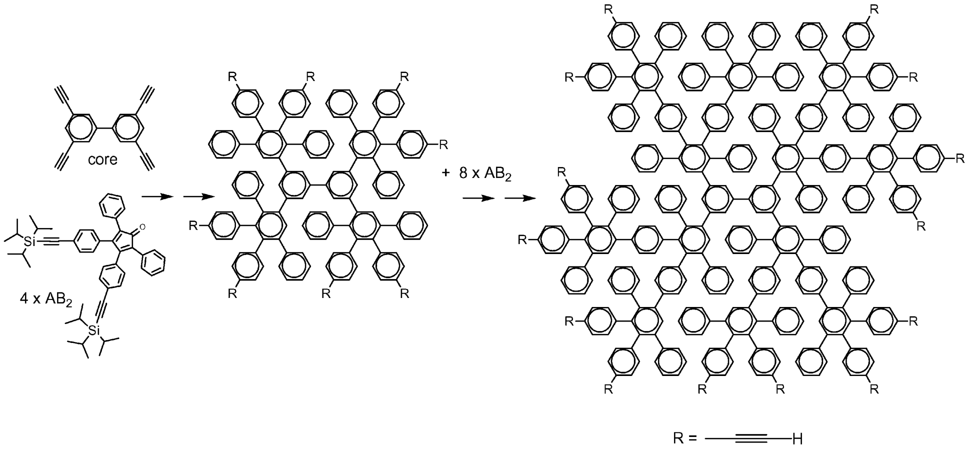


Scheme 1 Examples for some cycloaddition reactions employed for the synthesis of dendritic macromolecules.

In the synthesis of dendritic polymers so far mostly the [2 + 2 + 2] (reaction of three alkynes), the [4 + 2] CA (Diels–Alder: cyclopentadione + alkyne or maleimide) and the 1,3-dipolar CA (alkyne + azide or bisazine + maleimide) have been used. Scheme 1 exemplifies the mainly used reactions schematically.

Cycloaddition reactions and polyarylenes

Polyphenylenes are an interesting class of materials due to a usually high thermostability and chemical inertness. Furthermore, the highly aromatic nature renders these structures suitable for a number of technological applications *e.g.* in microelectronics implying also the potential to include controllable conductive behavior. Early on, CA reactions were



Scheme 2 Divergent synthesis of polyphenylene dendrimers through Diels–Alder reaction adapted from Müllen and co-workers.[15]

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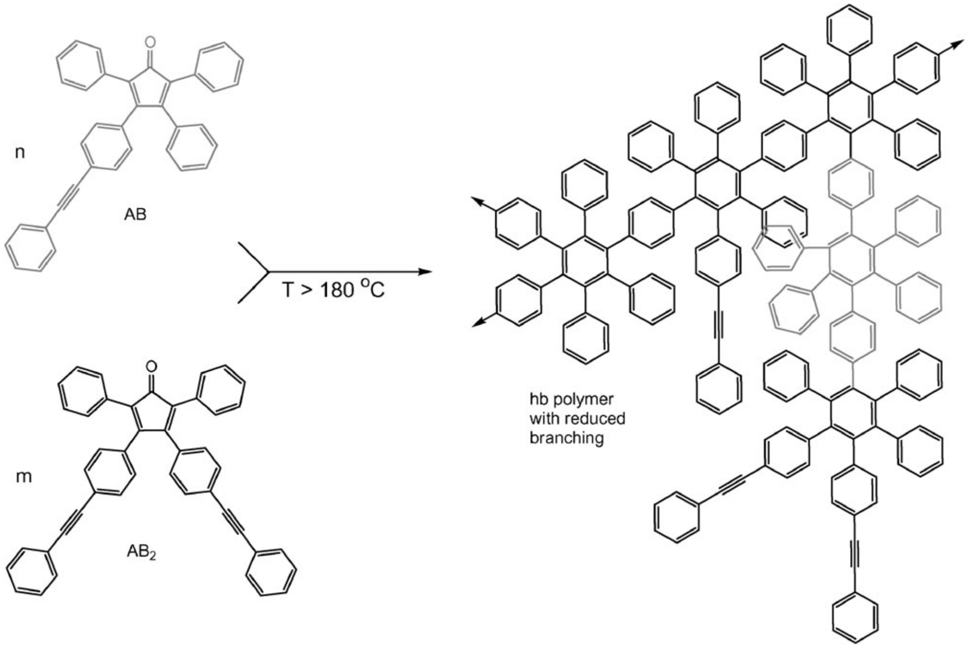

Scheme 3 Synthesis of hyperbranched polyphenylenes with an increased fraction of linear units by Diels–Alder reaction from AB_2 and AB monomers (adapted from ref. 50).

employed also for the preparation of linear polyphenylenes, exemplified mostly by work reported by Stille *et al.*[26,27]

Introducing branched units allows to overcome a major drawback of these structures, which is the limited processibility. Already in 1992 Miller *et al.*[28] reported the synthesis of perfectly branched polyphenylene dendrimers and their fluorinated analogues by a palladium-catalyzed coupling of arylboronic acids to 3,5-dibromo-1-(trimethylsilyl)benzene. But polyphenylene dendrimers based on the Diels–Alder reaction had been the issue of one of the first reports on the use of CA reactions in dendrimer synthesis.[14–16] This synthetic approach is based on the cycloaddition of phenylated cyclopentadienones with phenylated alkynes and subsequent decarbonylation (see Scheme 1). In an early attempt, Wiesler and Müllen[29] have used a convergent approach using 2,3,4,5-tetraphenylcyclopenta-2,4-dienone with 4,4′-diethynylbenzil to form the first-generation dendritic precursor which was further reacted with 1,3-diphenylacetone leading to the first generation dendron. However, this convergent approach was limited to the second generation, and thus, a divergent approach was employed for higher generation dendrimers as outlined in Scheme 2.[15] The AB_2 compound 3,4-bis(4-(triisopropylsilylethynyl)phenyl)-2,5-diphenylcyclopentadienone was added to a multifunctional alkyne core molecule in the corresponding amount. After deprotection of the alkyne units in the resulting first-generation dendrimer by treatment with *e.g.* ammonium fluoride and catalytic amounts of tetrabutylammonium fluoride in THF, the reaction steps are repeated to yield the second generation dendrimer and so on.

By now a vast number of polyphenylene dendrimers with a dense packing or a more extended arrangement of benzene rings, but also including additional extended or asymmetric structural units and a variety of functional surface groups had already been prepared and characterized.[15,16,30–38] Three-dimensional polyphenylene dendrimers are shape-persistent,[36] spherical molecules, whose structural properties allow spatial definition and topological isolation of functional groups in the center, in the dendritic scaffold, and at the periphery which renders them very interesting materials even in areas such as gene transfer or diagnostics. For examples, desymmetrized polyphenylene dendrimers[37] were prepared by the same [4 + 2] cycloaddition reaction employing monofunctionalized cyclopentadienones with polar groups as core moieties. By this, first it was possible to identify the different regioisomers which are a result of the mechanism of the Diels–Alder reaction, and secondly, these structures can be considered as the base for preparing new nanoamphiphiles. In addition, further oxidative cyclohydrogenation of the discussed polyphenylenes allows the construction of polycyclic hydrocarbon architectures,[14,16] and also the preparation of graphite-analogue thin layers and carbon nanotubes has been reported.[38,39] Dendritic polyphenylenes, modified with suitable end functionalities, have been already successfully employed in sensorics, *e.g.* in gold nanoparticle composite layers used in chemoresistor sensors.[40–42]

Soon not only the perfectly branched dendrimers, but also hyperbranched polyphenylenes had been explored. In general, polyphenylenes possess a high thermal and chemical stability. However, in contrast to their linear analogues, the hyperbranched polyphenylenes are non-conducting polymers, because an extended π-conjugation is hindered due to their tightly packed and strongly twisted phenylene units.[16] They show good solubility and processibility comparable to those of the corresponding dendrimers[43] but are more easily available also in larger quantities. Due to the outlined properties hyperbranched polyphenylenes are promising candidates for the application as insulating materials in microelectronics, where features like high thermal stability, good processibility

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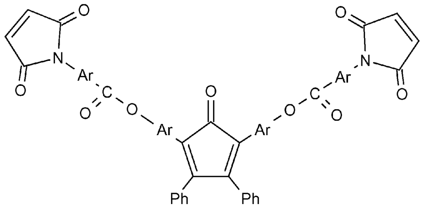


Scheme 4 AB_2 monomer employed by Harrison and Feast[52] for the preparation of hyperbranched poly(arylimide ester)s *via* a [4 + 2] cycloaddition reaction.

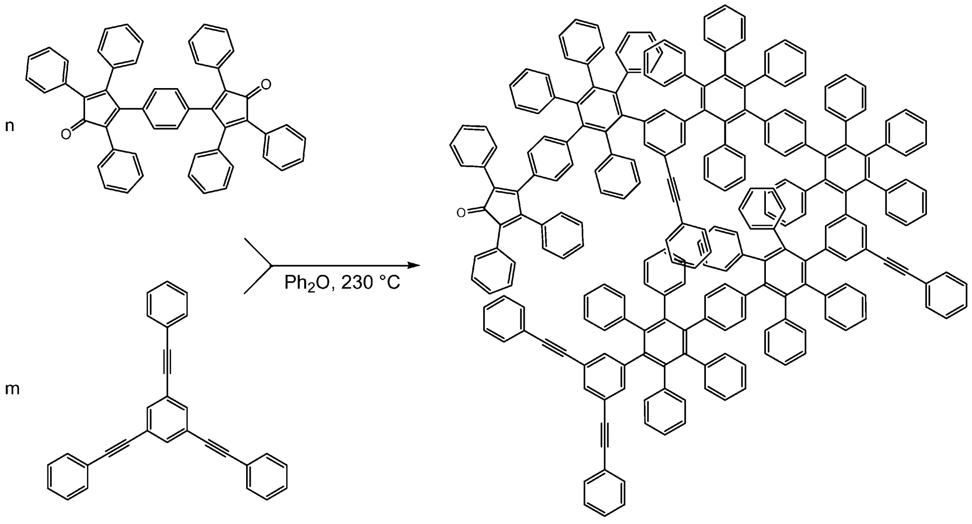
and solubility and low moisture absorption are required. An example for a low-dielectric-constant polymer based on branched and crosslinked polyarylenes which is already used by the semiconductor industry is SiLK™ from The Dow Chemical Company.[44,45]

The first hyperbranched polyphenylenes were synthesized by Kim and Webster starting from (3,5-dibromophenyl)boronic acid and dihalophenyl Grignard reagents *via* Pd(0) and Ni(II)-catalyzed aryl–aryl coupling reactions, respectively.[46] Müllen and co-workers,[47–49] however, reported the Diels–Alder reaction of the AB_2 monomer 3,4-bis(4-(triisopropylsilylethynyl)phenyl)-2,5-diphenylcyclopentadienone (Scheme 2) or 3,4-bis(4-(phenylethynyl)phenyl)-2,5-diphenylcyclopentadienone (see Scheme 3). 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^{-1} and broad polydispersity.[47]

This approach has been extended recently by combining the also the AB_2 monomer 3,4-bis(4-(phenylethynyl)phenyl)-2,5-diphenylcyclopentadienone with an AB monomer, the reaction was carried out in diphenyl ether at 230 °C (Scheme 3). Besides giving some control over the degree of branching in the branched polyphenylenes,[50] 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^{-1} were obtained compared to up to 600 000 g mol^{-1} for pure AB_2 monomer used under identical reaction conditions.[50] Unfortunately, even though all the repeating units—linear, dendritic and terminal—could be identified and proven, a quantification *e.g.* by ^{13}C NMR analysis is not possible due to overlapping signals, and thus, no quantitative information on the degree of branching can be given. The achievement of high molar masses with relatively broad molar mass distributions ($\bar{M}_w/\bar{M}_n$ between 3 and 30) and rather multimodal GPC traces combined with an excellent solubility *e.g.* in chloroform or toluene are further indications for a highly branched nature of the products.[50] In addition, solid state[36] and solution[51] NMR studies proved hindered dynamics in the dendritic polyphenylenes as a result of the dense packing of the phenylene rings.

Harrison and Feast[52] reported the preparation of highly soluble hyperbranched polyarylimides using also 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 might be further oxidized to a benzimide unit. Unfortunately, no further characterization details of the products are given. Scheme 4 features one of the used AB_2 monomers, the diester monomer, similarly, a diamide monomer was successfully applied. The resulting polymers from the diester monomer were soluble in chloroform, acetone and THF whereas those from the diamide AB_2 compound showed limited solubility at higher molar masses probably due to strong hydrogen bonding.

There are two ways to prepare hyperbranched polymers: the classical "Flory" approach using AB_x type monomers as a non-gelating system, and the more simple $A_2 + B_3$ approach which allows the use of more easily available monomers but implies the possibility of gelation which is only avoided by restriction of the conversion or high imbalance of the stoichiometry. Nevertheless, also by the $A_2 + B_3$ approach fully soluble hyperbranched polyphenylenes *via* the Diels–Alder reaction have been prepared[50] following the route demonstrated extensively by Müllen and co-workers.[16] Scheme 5 indicates the monomers used. It is interesting to note that by



Scheme 5 Synthesis of hyperbranched polyphenylenes by the $A_2 + B_3$ approach (Diels–Alder reaction).

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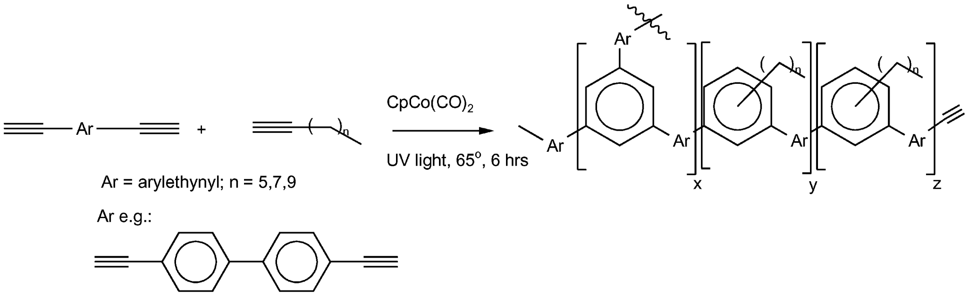

Scheme 6 Synthesis of hyperbranched polyarylethynyls by [2 + 2 + 2] cobalt catalyzed phototrimerization (adapted from refs. 13 and 54).

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this monomer combination a 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[51] revealed that the formation of linear units is favored since the reactivity of the third B unit in B_3 after two B's have already reacted is reduced. Only when high excess of A_2 is applied the formation of dendritic units becomes more significant, however, then the achievable molar mass is limited. An advantage of this fact is that also the critical conversion is shifted by this reduced reactivity and thus, only fully soluble products were obtained under the applied conditions.

Hyperbranched polyphenylenes and -arylenes are also prepared by [2 + 2 + 2] cycloaddition reactions as reported by Tang and co-workers.[53–57] Here, the diyne polycyclotrimerization initiated by transition-metal catalysts[53–56] (Scheme 6) and base-catalyzed alkyne polycyclization is applied.[56,57] In the first case, a variety of bifunctional arylene ethynylene and monofunctional alkyne monomers were combined and tantalum, niobium or cobalt catalysts were used. An optimization of the monomer combination was necessary before the system shown in Scheme 6,[54] with $n = 5$ in the alkyne monomer and under irradiated cobalt catalysis, resulted in highly soluble highly branched materials with $\bar{M}_w = 20\,000$ g mol^{-1} and an extremely high thermal stability ($T_{decomp} > 580$ °C). In this approach, the addition of the mono-alkyne avoids gelation and induces flexibility into the system leading finally to soluble products. Due to the UV irradiated cobalt catalysis, the polymerization results in a random mixture of 1,2,4- and 1,3,5-trisubsituted 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 could be 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(aroylarylene)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^{-1}.[56,57] Here, bis(aroylacetylene)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 from the disappearance of any remaining alkyne units. These polymers, again fully soluble in common organic solvents, showed high photosensitivity and were readily photocrosslinked to give photoresist patterns with nanometer resolutions. This demonstrates nicely the high potential of cycloaddition reaction in the synthesis of new dendritic polymers with potential use in high performance applications.

In addition to the [2 + 2 + 2] cyclotrimerization reaction being able to be used to prepare branched polyphenylenes it can also allow also to combine effectively perfectly branched monodendrons when suitable units are incorporated as the focal point. Thus, Fréchet and Hecht[58] incorporated acetylenic focal units into polyaromatic ether dendrons (so-called Fréchet-type dendrons) which then allowed to combine three of the dendrons in toluene under cobalt catalysis *via* the [2 + 2 + 2] cycloaddition reaction by the formed benzene unit (Scheme 7). Even though the yields dropped to 36% when higher generation dendrimers were used, due to the very clean trimerization reaction only the desired products were obtained, which could easily be separated from the unreacted dendrons.

The high versatility already demonstrated so far for the [4 + 2] and [2 + 2 + 2] CA reactions for the preparation of perfectly branched dendrimers as well as hyperbranched or highly branched polymers combined with the interesting property profile of the resulting products, *e.g.* the combination of high rigidity and high content of aromatic units (leading to high thermo- and chemostability) with easy processibility, allows the assumption that we will see more interesting polymer architectures produced by this approach.

Complex dendritic architectures by 1,3-dipolar cycloaddition reactions

Whereas the above outlined Diels–Alder reactions and [2 + 2 + 2] cyclotrimerization reactions are specially well suited to prepare highly aromatic hydrocarbon structures which exhibit high shape-persistancy and usually a more non-polar 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, a high stereocontrol is possible and the formation of specific intermediates may allow to influence 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 re-arrangements (*e.g.*

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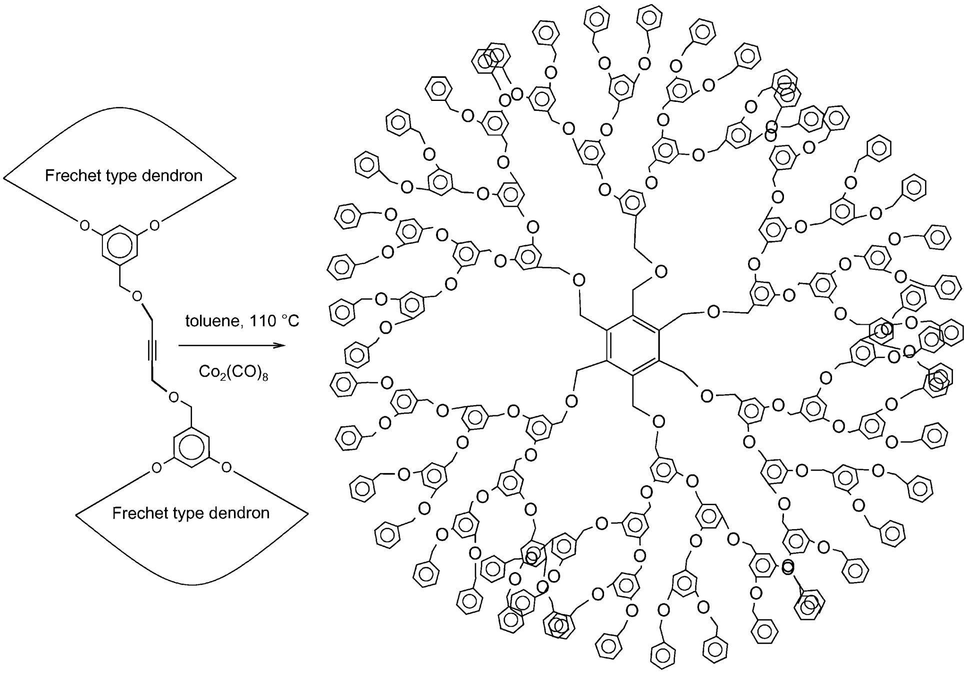


Scheme 7 Dendron core coupling through [2 + 2 + 2] cycloaddition reaction.[58]

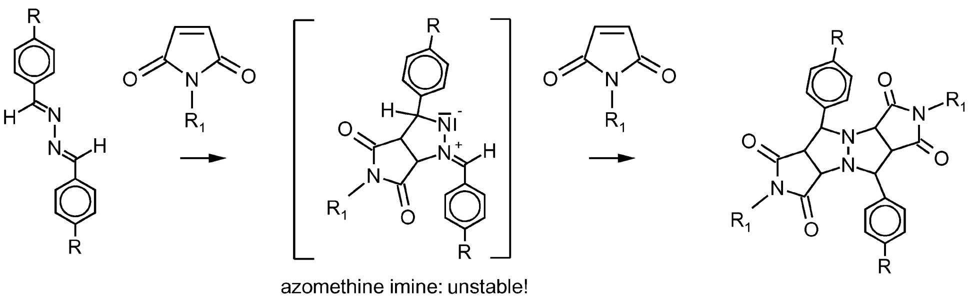
sigmatropic shifts), and therefore, the reaction conditions have to be selected carefully.

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. One is the reaction of organic azides with alkynes forming a triazole ring, which experienced an enormous revival in many fields of polymer science after Sharpless[20,21] and others[59–61] pointed out that under suitable copper catalysis complete control of the regioselectivity can be achieved. This, in combination with easy accessibility of the monomers, very high yields, and the insensitivity of the cycloaddition reaction towards many functional groups which led to the term "click chemistry",[20,21] is the base for the huge success of this CA reaction.

The other approach used so far for the preparation of dendritic structures is based on the so-called "criss-cross" cycloaddition of bisazines[62] which always react in a two step dual (3 + 2) cycloaddition *via* an instable azomethine imine 1,3-dipole intermediate (Scheme 8).[63]

"Criss-cross cylcoaddition"

This reaction was used already by Stille and Anyos[12] and later by Maier and co-workers[64,65] for the synthesis of a variety of linear heterocyclic polymers, some based on hexafluoroacetone azine which is highly reactive and permits polymerizations at room temperature with high regioselectivity.[66] Maier, Voit and co-workers[67,68] extended the use of the criss-cross cylcoaddition 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 synthetically realized. Due to the special features of that reaction and the instable azomethine imine intermediate it was possible to achieve hyperbranched polymers 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 instable 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 to go backwards to the starting material. Since the linear units are not stable, they cannot be found in the final product and



Scheme 8 Formation of a tetracyclic system by 1,3-dipolar cycloaddition reaction of bisazines with maleimides passing through an instable azomethine imine intermediate.

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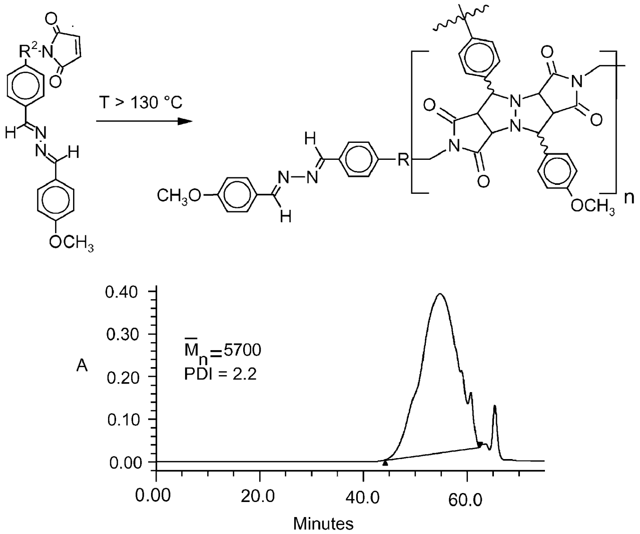


Scheme 9 Hyperbranched polymers with a degree of branching of 100% prepared by 1,3-dipolar cycloaddition of a bisazine-maleimide AB_2 monomer: GPC proves the formation of broadly distributed hyperbranched oligomeric products with $\bar{M}_n$ about 5000 g mol^{-1} (according to calibration with linear standards) (adapted from ref. 67).

only bisazine terminal units as well as tetracyclic fully dendritic units were determined 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.[69]

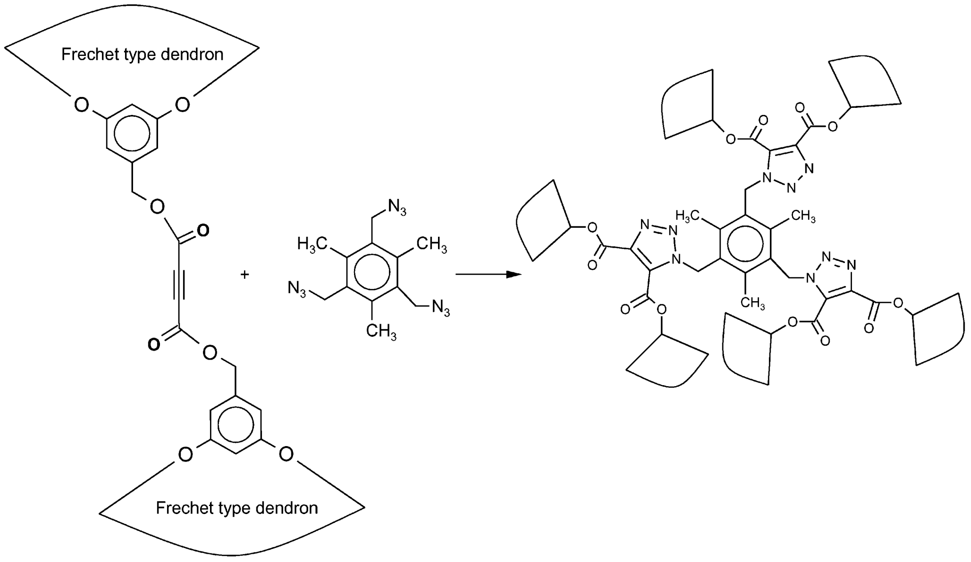
Nevertheless, irregularly branched products of molar masses $\bar{M}_w$ up to 10 000 g mol^{-1} and polydispersities around 2.5 (Scheme 9) were isolated and certainly qualified as "hyperbranched".[67] This result is similar as the one reported for the regioselective cyclotrimerization[56] and also Smet *et al.*[70] were also able to prepare hyperbranched polymers with a degree of branching of 100%, but they used the acid catalyzed condensation of isatin with aromatic compounds—no cycloaddition reaction—leading to hyperbranched polyaryleneoxindoles.

"Click chemistry"

In the field of 1,3-dipolar cycloadditions a very flexible reaction is the addition of organic azides to internal and terminal triple bonds forming triazole rings with the excellent potential to prepare a variety of perfectly branched dendrimers. In addition, it allows for extremely versatile modification reactions, provides the chance for unusual architectures by "clicking together" building blocks and even leads to totally new hyperbranched polymers. This 1,3-dipolar cycloaddition reaction, described first by Huisgen *et al.*[18] but promoted recently as click chemistry by Sharpless and co-workers,[20,21] was explored very successfully in dendrimer synthesis and functionalization.[71,72] 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 and co-workers[21] and Tornoe *et al.*[60] pointed out that the *anti*-regioisomer is formed solely using a copper-mediated CA reaction. Unfortunately, this stereocontrol can not be achieved when internal triple bonds are involved in the reaction.

Linear poly(triazole)s have been prepared by Baldwin and co-workers.[73] as early as 1966, but more recently, after "click chemistry" became so fashionable, the 1,3-dipolar CA was also used to postmodify linear polymers having pendant alkyne groups or to combine two polymer segments *via* end group "clicking" to prepare block copolymers (examples, see refs. 74–77).

Dehaen and co-workers[71] were among the first to use the 1,3-dipolar CA reaction for a convergent approach towards heterocyclic dendrimers. First, the heterocyclic triazole ring was only introduced in the final step when the Fréchet type polyaromatic ether dendrons, which were modified with an acetylenedicarboxylate moiety, were finally coupled to a triazide (Scheme 10). The reaction was carried out at 70 °C for several days to achieve complete conversion as proven by spectroscopic means. Nevertheless, the problem of incomplete



Scheme 10 Attachment of Fréchet type dendrons with an acetylenic focal unit to a trivalent azide core by 1,3-dipolar cycloaddition reaction.[71]

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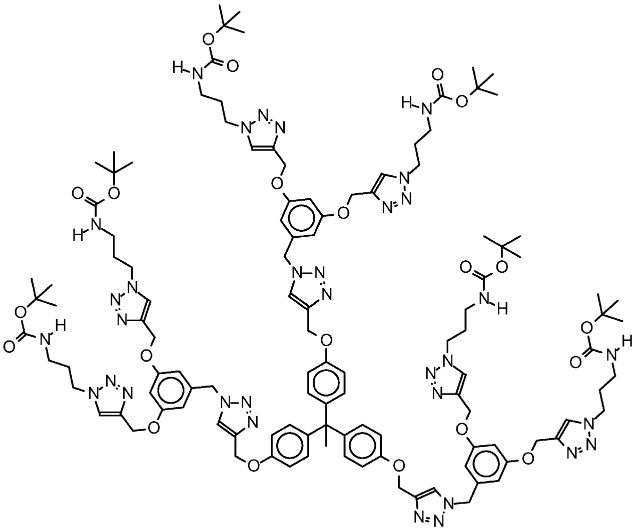


Scheme 11 End-functionalized poly(triazole) dendrimer of generation 1 prepared by "click chemistry".[72]

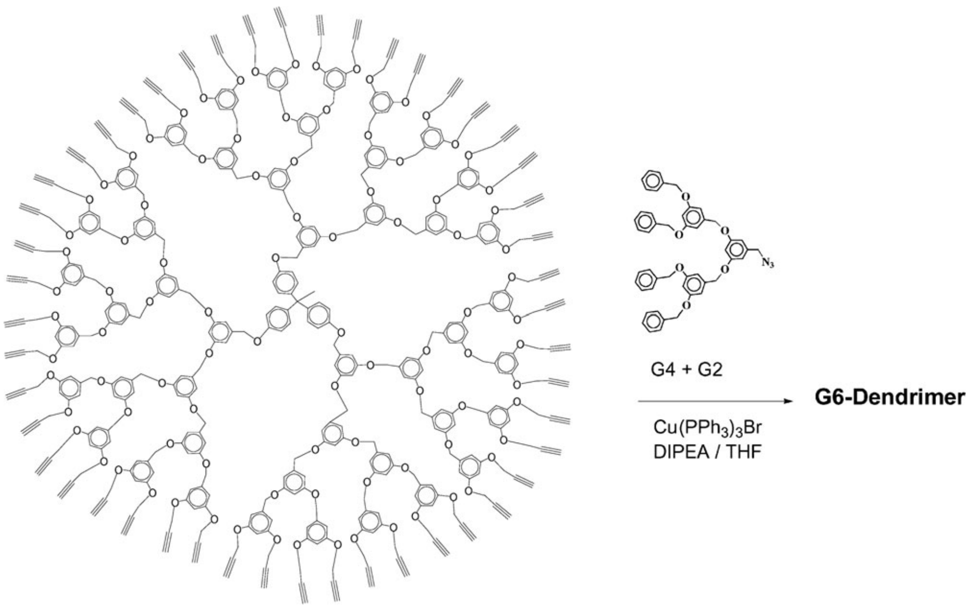
reaction occurred when dendrons of the third generation were used probably due to steric hindrance.

The incorporation of the triazole rings within the dendrons was reported also by the same group.[71] For that, diethylene glycol spacers between a peripheral azide and a protected core alkyne moiety were introduced. The azide was then reacted with acetylenecarboxylate ester resulting in the formation of an internal triazole ring and peripheral ester groups. After deprotection the focal alkyne unit was then again reacted with a hexafunctional azide core leading to the desired dendrimers.

Lee *et al.*[78–82] reported also recently a "convergent" type synthesis of dendrimers, symmetric ones and unsymmetric ones, by coupling of suitable alkyne focal units of dendrons to azide cores or *vice versa*, similar as described by Dehaen and co-workers[71] (Scheme 10) demonstrating the high versatility. But clearly, the potential given by the combination of click chemistry and dendritic structures is marvellously and extensively demonstrated by Hawker and co-workers,[72,83,84] Sharpless and co-workers[85] and Frechet and co-workers.[86] First, the 1,3-diploar cycloaddition reaction of azides with terminal alkynes was used directly to build up dendrons of different generation by a convergent[72] and a divergent[83] approach. Secondly, terminal alkyne groups in the periphery could be modified easily with readily available functional azides for the introduction of a broad variety of functional end groups including unprotected acid and alcohol groups, protected amines, polar ethylene glycol units, sugar units, nucleosides, dyes, bulky adamantyl groups, and so on.[72,83,84,86] Scheme 11 is presenting a low generation simple example out of those vast structures reported.

It is important to note that in this case a relative simple catalytic system was involved by using $CuSO_4$ and sodium ascorbate which create the necessary Cu^I species. The reaction can be carried out in any kind of polar solvent including water, impurities within the solvent or the monomers are usually of no concern, the reaction is quantitative and purification is easily achieved due to the absence of any side products. When the solubility of the starting components or the products was not high enough in water or alcohols, THF could be employed as solvent using $(PPh_3)_3CuBr$ as catalyst system and the efficiency of the reaction could be further improved when microwave heating was applied.[83,84] This shortened also dramatically the reaction times to sometimes only a couple of minutes. These features are ideal in dendrimer synthesis.

Not only dendrimer build up and end group post-modification was successfully demonstrated but also the attachment of a G2 and even a G3 dendron to a G4 dendrimer having alkyne groups in the periphery in a divergent approach (Scheme 12).[84] Here, again microwave irradiation proved very efficient, thus



Scheme 12 Preparation of a G6 dendrimer *via* grafting of G2 azide functionalized dendrons onto an alkyne modified G4 dendrimer (adapted from Hawker and co-workers).[84]

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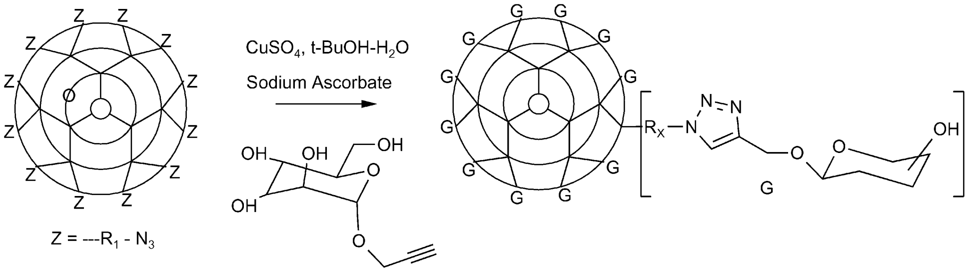

Scheme 13 Postmodification of azide modified dendrimers with unprotected alkyne functionalized sugar moieties leading to glyco-dendrimers (adapted from Riguera and co-workers[89]).

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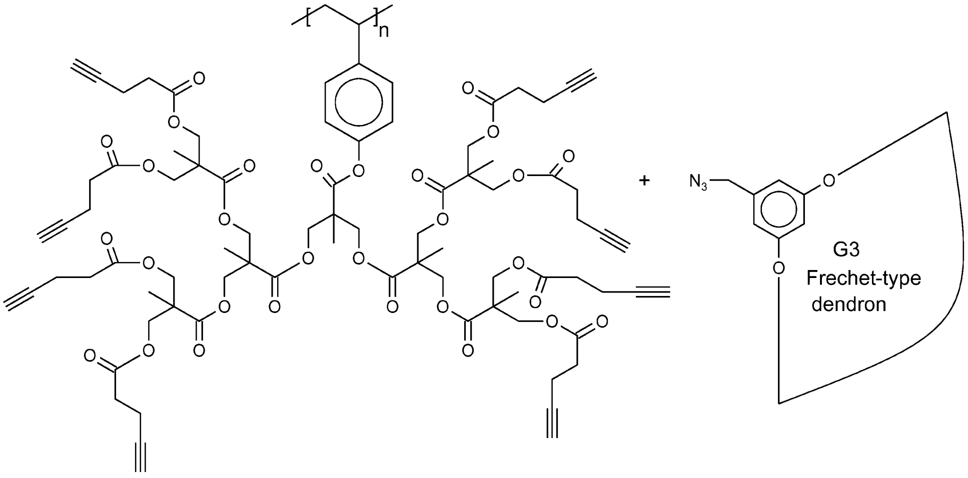
even for these very bulky reagents conversions of 95% (G2) and 75% (G3) could be achieved.

The possibility to have full control of the structure due to the highly efficient CA reaction under very mild reaction conditions and thus, to combine differently modified dendrons as building blocks like in a "Lego™" playground as well as to introduce a certain functionality selectively only to part of a dendrimer structure allows now to build up very complex and highly multifunctional structures. This is demonstrated again nicely by Hawker, Sharpless and co-workers when they produced multivalent, asymmetrical dendrimers containing *e.g.* 16 mannose units and two coumarin chromophores.[85]

Liskamp and co-workers[87] could show that the microwave assisted synthesis of multivalent dendritic peptides involving click chemistry also works highly efficient. Thus, bioactive oligopetides and cyclic peptides could be functionalized with azide groups and were then linked in high yields to alkyne end-functionalized dendritic structures in THF–water (1 : 1) at 100 °C (microwave irradiation, 10 min) in the presence of $CuSO_4$/Na-ascorbate. Similarly, a variety of azido carbohydrates, protected with benzyl or acetate groups and containing azide moieties, were coupled to alkyne functionalized dendrons (yields >90%) in DMF, under microwave irradiation at 80 °C for 20 min.[88] This approach towards highly biocompatible and even bioactive dendritic molecules was further expanded by Riguera and co-workers,[89] who demonstrated that also unprotected alkyne modified carbohydrate units can be easily linked to dendrimers having azide units in the periphery (Scheme 13). However, one problem not dressed in this area so far, might be residual copper within the products which needs to be fully removed before any biomedical application can be addressed.

Besides bioactive components, also other functional units can be easily incorporated into dendrimers *via* click chemistry postmodification, *e.g.* recently, ferrocenyl units were incorporated resulting in interesting senor materials[90] and specific electron transfer was studied in fullerene-ferrocene-dendrimer assemblies.[91]

The preparation of dendritic-linear hybrids using click chemistry has attracted also much attention recently. Thus, Fréchet and co-workers[92] used polyaromatic ether dendrons with azide focal units to decorate effectively poly(vinylacetylene) with pendent dendrons. At this point, only dendrons up to third generation could be attached in quantitative yield after long reaction times (still under conventional conditions). For higher generations steric hindrance was encountered. However, AFM proved already that the polymers decorated with G3 dendrons exhibit rigid rod like structures. In order to overcome the problem of steric hindrance close to the backbone of the linear polymer chain, a new approach was utilized: the coupling of dendrons on dendrons coupled to a linear polymer leading to doubly-dendronized linear polymers (Scheme 14).[86] For that poly(hydroxystyrene) was divergently dendronized with a dendritic poly(aliphatic ester) based on bishydroxypropionic acid up to generation 3. Then, postmodification with pentynoic acid was achieved providing



Scheme 14 Doubly dendronized polymers *via* click chemistry (adapted from Fréchet and co-workers).[86]

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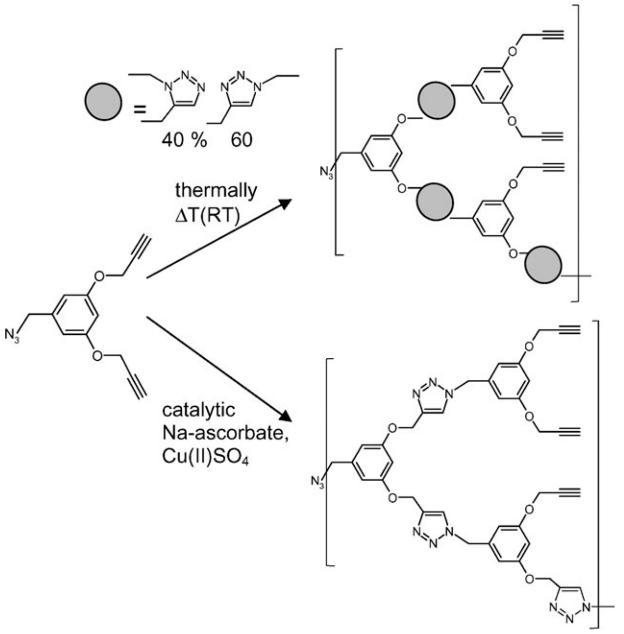
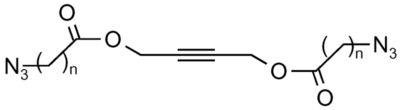


Scheme 15 Preparation of hyperbranched poly(triazole)s *via* Cu^I mediated and thermal 1,3-dipolar CA of 3,5-bis(progargyloxy)benzyl azide.[94]

terminal alkyne groups on that dendronized polymer. Click chemistry was applied to link G3-azide dendrons to theses pre-dendronized molecules finally producing a modification of the linear polymers with G6 dendrons (Scheme 14). A nearly quantitative dendronization of each repeating unit was assumed from GPC and spectroscopic evidence.

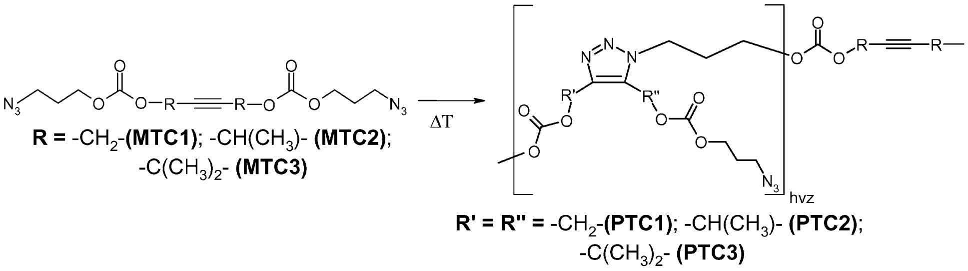
A new methodology for the preparation of well-defined core–shell nanoparticles was also developed employing click chemistry and dendrimers.[93] For that amphiphilic poly(acrylic acid)-*b*-poly(styrene) block copolymers had been assembled into micelles and were partially functionalized within the corona with alkynyl groups. Subsequently, a divergently grown first generation dendrimer with terminal azide functions was successfully employed as a multivalent crosslinker for the shell of the micelles, allowing the preparation of a very robust nanoparticle with some reactive alkynes in the outer shell which are suitable for further functionalization.



Scheme 16 AB_2 bisazide ester monomer described by Smet *et al.*[95] for the synthesis of hyperbranched poly(triazole)s *via* thermal 1,3-dipolar CA.

As one can expect, the 1,3-dipolar CA reaction of azides and alkynes also entered 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).[94] The polymerization of the AB_2-bisalkyne was either conducted *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 maintained and only 1,4-substitution 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 ^1H 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 (Scheme 15). The 1,4- and 1,5-substitutions in the triazole ring were found in a 64 : 36 ratio.

Bisazides with internal triple bonds as AB_2 monomers for the synthesis of hyperbranched poly(trizaoles) have been independently developed by Voit and co-workers[94] and Smet *et al.*[95] 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 1,3-dipolar CA reaction will occur leading again to a mixture of 1,4- and 1,5-substituted triazoles. Smet *et al.*[95] studied some ester-alkyne-diazides (Scheme 16). Here, only oligomers could be obtained from the AB_2 monomer with $n = 1$ and the products showed a tendency to gel after storage, probably because of some decomposition of the azide groups. Thus, subsequently the azide end groups were transformed into the corresponding amines and further acylated with stearyl chloride which led to a fully soluble product. However, purification and isolation of all obtained oligomers proved difficult due to their oily appearance. In a further step, it was tried to produce an AB_2 monomer with an more activated acetylenedicarboxylate unit. Unfortunately, the still protected precursor of the resulting monomer containing a dibromofumaric ester unit started already to polymerize during transformation in the acetylenedicarboxylic ester in refluxing THF and rapid cross-linking of the materials was observed allowing only the observation of some small soluble oligomers by NMR.



Scheme 17 Synthesis of hyperbranched poly(triazole)s PTC1–3 from the AB_2 bisazide carbonates MTC1–3 *via* thermal 1,3-dipolar CA.[94]

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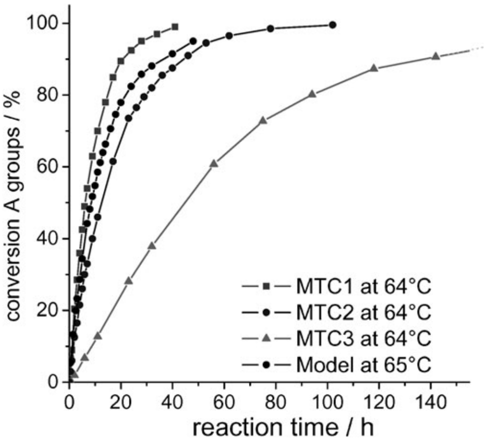

Fig. 1 Dependency of the conversion of A groups on the reaction times for the different AB_2 bisazide carbonates MTC1–3. The model reaction is based on the addition reaction of 3-azidopropanol to 1,4-diacetoxybut-2-inyl (adapted from ref. 96).

Voit and co-workers[94] were able to achieve fully soluble products by low temperature (45 °C) autopolymerization in bulk even of high molar mass ($\bar{M}_n = 10\,000$ g mol^{-1}) from the AB_2 bisazido monomer MTC1 shown in Scheme 17.

Full structural analysis is complex due to the large number of possible isomeric structural units, but the highly branched structure could be verified in the products and a degree of branching of 50% can be assumed. The resulting product bears a large number of highly reactive azide groups which can give rise to a large spectrum of further end-group modification. Here, it is most suitable to use the reaction with functional terminal alkynes again for the postmodification due to the easy and highly efficient reaction. By this it was possible to introduce a variety of polar and unpolar end groups which allow firstly to avoid any side reactions of the azide units and secondly, to adjust the polarity of the material *e.g.* in order to achieve better solubility in unpolar solvents.[96] Polymers based on MTC1–3 have aliphatic carbonate groups in their structure. Aliphatic carbonates are known to decompose readily at temperatures around 200 °C. This makes these hyperbranched polymers to promising materials *e.g.* for the use as porogens for the preparation of nanoporous materials but this also requires to find a suitable solvent for both, porogen and matrix material, for the successful preparation of homogenous films.[96]

In more extended studies[96] it was finally possible to optimize the reaction conditions, and also soluble products could be obtained for MTC2 and MTC3. The reactivity of these two compounds is significantly lower than the one of MCT1 as it was found in some kinetic studies (Fig. 1) carried out at 64 °C. For MTC3 the reaction temperature should not be increased above 45 °C due to the high thermolability of the carbonate units and thus some degradation was observed during the kinetic experiment at 64 °C. However, at 45 °C reaction times of up to four weeks had to be employed to achieve high molar mass products. The evaluation of the data achieved at 64 °C for first- and second-order kinetics showed, that in this AB_2 CA reaction none of these plots showed ideal linear behavior. It looks like that in the beginning of the reaction the expected second order dependency was valid and later on a first-order dependency took over. Detailed evaluation of this behavior and also a very close study of the accompanying development of the molar masses and the polydispersity led to the conclusion that internal cyclization takes place to a significant proportion at high conversion of functional group. It has to be noted that during these studies it could be verified that soluble products with $\bar{M}_n$ up to 38 000 g mol^{-1} and $\bar{M}_w$ = 100 000 g mol^{-1} (MALLS detection) can be produced from MTC1. Fig. 2 exemplifies a molecular modeling result for the hyperbranched polymer PTC1 with a degree of polymerization of 110 showing a highly branched but still relatively open, irregular structure with dimensions of 19 × 13 × 10 nm.[96]

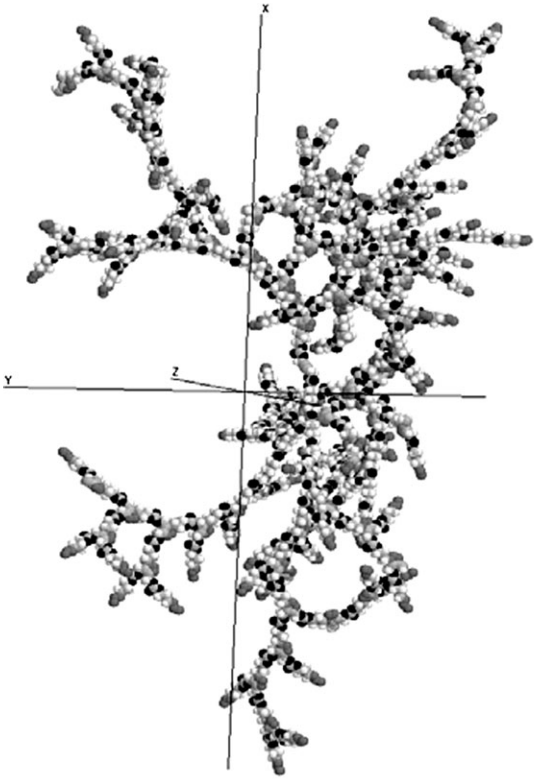

Fig. 2 Molecular modeling result for PTC1 (in vacuum) having a degree of polymerization P_n = 110 (dimensions: x = 19 nm, y = 13 nm, z = 10 nm) (adapted from ref. 96).

Since it is still rather difficult to produce hyperbranched polymers *via* the AB_2 approach due to the high reactivity of the functionalities and thus problems of monomer isolation and the danger of premature polymerization, it looks like the 1,3-dipolar CA of alkynes with azides by the $A_2 + B_3$ approach will enter the field of technical branched products more easily, mainly because suitable A_2 and B_3 monomers are relatively easily available. Here, Finn and Diaz[97] 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). The products obtained had very good adhesive properties and significantly outperformed commercial adhesives.

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Outlook

Cycloaddition reaction entered, with a few exception, only recently the field of dendritic polymers. Nevertheless, due to the resulting high yields, high selectivity, very clean reactions and often the absence of any side reaction, they proved already extremely versatile and ideal for the effective dendrimer synthesis as well as highly efficient for the post-modification of dendritic highly functional macromolecules. Especially two types of reactions are very promising: the Diels–Alder reaction of cyclopentadienone with alkynes leading to a large variety of otherwise very difficult to realize polyarylene dendrimers and the 1,3-dipolar cycloaddition reaction of azides with alkynes. The later allows not only the preparation of fully new dendritic structures, it is also very efficient in order to introduce complex functionality into dendritic structures.

The so far limited variety of CA reaction used in the synthesis of dendritic polymers points also to the rather unlimited potential which still can be explored. Necessary requirements, however, are reasonable good availability of the needed starting compounds as well as sufficient stability of the reactive functionalities used in the CA reactions. With this in mind, it can be expected that the field will expand very rapidly leading to beautiful new dendritic architectures but also allowing for very effective synthesis procedures which might promote the commercialization of dendritic molecule for high-tech applications.

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References

1 G. R. Newkome, C. N. Moorefield and F. Vögtle, *Dendrimers and Dendrons: Concepts, Synthesis, Applications*, Wiley-VCH, Weinheim, 2001.
2 J. M. J. Fréchet and D. A. Tomalia, *Dendrimers and Other Dendritic Polymers*, John Wiley & Sons, Chichester, UK, 2001.
3 A. Hult, M. Johansson and E. Malmström, in *Advances in Polymer Science*, ed. J. Roovers, Springer Verlag, Berlin Heidelberg, 1999, vol. 143, p. 1ff.
4 Y. Kim, *J. Polym. Sci., Part A: Polym. Chem.*, 1998, **36**, 1685.
5 D. A. Tomalia and J. M. J. Fréchet, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**, 2719.
6 S. Hecht, *J. Polym. Sci., Part A: Polym. Chem.*, 2003, **41**, 1047.
7 K. Inoue, *Prog. Polym. Sci.*, 2000, **25**, 453.
8 J. M. Jikei and M. Kakimoto, *Prog. Polym. Sci.*, 2001, **26**, 1233.
9 C. Gao and D. Yan, *Prog. Polym. Sci.*, 2004, **29**, 183.
10 C. R. Yates and W. Hayes, *Eur. Polym. J.*, 2004, **40**, 1257.
11 B. Voit, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 2679.
12 J. K. Stille and T. Anyos, *J. Polym. Sci., Part A: Gen. Pap.*, 1964, **2**, 1487.
13 G. W. Goodall and W. Hayes, *Chem. Soc. Rev.*, 2006, **35**, 280.
14 M. Müller, H. Mauermann-Düll, M. Wagner, V. Enkelmann and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1583.
15 (*a*) F. Morgenroth, E. Reuther and K. Müllen, *Angew. Chem.*, 1997, **109**, 647; (*b*) F. Morgenroth, E. Reuther and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 631.
16 A. J. Berresheim, M. Müller and K. Müllen, *Chem. Rev.*, 1999, **99**, 1747.
17 L. J. Hobson and W. J. Feast, *Chem. Commun.*, 1997, 2067.
18 R. Huisgen, G. Szeimies and L. Moebius, *Chem. Ber.*, 1967, **100**, 2494.
19 A. Padwa, *1,3-Dipolar Cycloaddition Chemistry*, Wiley, New York, 1984.
20 H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004.
21 V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2002, **41**, 2596.
22 I. Flemming, *Pericyclic Reactions*, Oxford University Press, Oxford, 1999.
23 R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag Chemie, GmbH, Weinheim, 1970.
24 W. Carruthers, *Cycloaddition Reactions in Organic Synthesis*, Pergamon Press, Oxford, 1999, and literature cited therein.
25 R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 321.
26 J. K. Stille, F. W. Harris, R. O. Rakutis and H. Mukamal, *J. Polym. Sci., Part B: Polym. Lett.*, 1966, **4**, 791.
27 J. K. Stille, R. O. Rakutis, H. Mukamal and F. W. Harris, *Macromolecules*, 1968, **1**, 431.
28 Th. M. Miller, T. X. Neenan, R. Zayas and H. E. Bair, *J. Am. Chem. Soc.*, 1992, **114**, 1018.
29 U.-M. Wiesler and K. Müllen, *Chem. Commun.*, 1999, 2293.
30 U.-M. Wiesler, A. J. Berresheim, F. Morgenroth, G. Lieser and K. Müllen, *Macromolecules*, 2001, **34**, 187.
31 U.-M. Wiesler, T. Weil and K. Müllen, *Top. Curr. Chem.*, 2001, **212**, 1.
32 A. C. Grimsdale and K. Müllen, *Angew. Chem., Int. Ed.*, 2005, **44**, 5592.
33 U. M. Wiesler, A. J. Berresheim, F. Morgenroth, G. Lieser and K. Müllen, *Macromolecules*, 2001, **34**, 187.
34 S. Loi, H. J. Butt, C. Hampel, R. Bauer, U. M. Wiesler and K. Müllen, *Langmuir*, 2002, **18**, 2398.
35 E. V. Andreitchenko, C. G. Clark Jr., R. E. Bauer, G. Lieser and K. Müllen, *Angew. Chem., Int. Ed.*, 2005, **44**, 6348.
36 M. Wind, U.-M. Wiesler, K. Saalwächter, K. Müllen and H. W. Spiess, *Adv. Mater.*, 2001, **13**, 752.
37 G. Mihov, I. Scheppelmann and K. Müllen, *J. Org. Chem.*, 2004, **69**, 8029.
38 V. S. Iyer, K. Yoshimura, V. Enkelmann, R. Epsch, J. Rabe and K. Müllen, *Angew. Chem.*, 1998, **110**, 2843.
39 L. Zhi, J. Wu, J. Li, M. Stepputat, U. Kolb and K. Müllen, *Adv. Mater.*, 2005, **17**, 1492.
40 M. Schlupp, T. Weil, A. J. Berresheim, U. M. Wiesler, J. Bargon and K. Müllen, *Angew. Chem., Int. Ed.*, 2001, **40**, 4011.
41 T. Vossmeyer, B. Guse, I. Besnard, R. E. Bauer, K. Müllen and A. Yasuda, *Adv. Mater.*, 2002, **14**, 238.
42 N. Krasteva, I. Besnard, I. B. Guse, R. E. Bauer, K. Müllen, A. Yasuda and T. Vossmeyer, *Nano Lett.*, 2002, **2**, 551.
43 A. J. Berresheim, F. Morgenroth, U. M. Wiesler and K. Müllen, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 1998, **39**, 721.
44 S. J. Martin, J. P. Godschalx, M. E. Mills, E. O. Shaffer II and P. H. Townsend, *Adv. Mater.*, 2000, **12**, 1769.
45 J. P. Godschalx, D. R. Romer, Y. H. So, Z. Lysenko, M. E. Mills, G. R. Buske, P. H. Townsend III, D. W. Smith, Jr., S. J. Martin and R. A. Devries, Dow Chemical Company USA, Polyphenylene oligomers and polymers, *US Pat.*, 5,965,679, 1999.
46 Y. H. Kim and O. W. Webster, *Macromolecules*, 1992, **25**, 5561.
47 F. Morgenroth and K. Müllen, *Tetrahedron*, 1997, **53**, 15349.
48 A. L. Rusanov, Z. B. Shifrina, E. G. Bulycheva, M. L. Keshtov, M. S. Averina, Y. I. Fogel, K. Müllen and F. W. Harris, *Macromol. Symp.*, 2003, **199**, 97.
49 A. L. Rusanov, M. L. Keshtov, P. V. Petrovskii, N. M. Belomoina, C. V. Keshtova, G. I. Timofeeva, I. A. Ronova, K. Müllen and F. Morgenroth, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1999, **5**, 953.
50 K. Stumpe, H. Komber and B. Voit, *Macromol. Chem. Phys.*, 2006, **207**, 1825.
51 H. Komber, K. Stumpe and B. Voit, *Macromol. Chem. Phys.*, 2006, **207**, 1814.
52 R. M. Harrison and W. J. Feast, *PMSE [Prepr.]*, 1997, **77**, 162.
53 H. Peng, K. Xu, J. Luo and B. Z. Tang, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 2001, **42**, 560.
54 K. Xu, H. Peng, Q. Sun, Y. Dong, F. Salhi, J. Luo, J. Chen, Y. Huang, D. Zhang, Z. Xu and B. Z. Tang, *Macromolecules*, 2002, **35**, 5821.

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55 H. Peng, J. W. Y. Lam and B. Z. Tang, *Macromol. Rapid Commun.*, 2005, **26**, 673.
56 H. Dong, R. Zheng, J. W. Y. Lam, M. Häußler and B. Z. Tang, *Macromolecules*, 2005, **38**, 6382.
57 M. Häußler, J. W. Y. Lam, R. Zheng, H. Peng, J. Luo, J. Chen, C. C. W. Law and B. Z. Tang, *C. R. Chim.*, 2003, **6**, 833, and references therein.
58 S. Hecht and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1999, **121**, 4084.
59 F. Perez-Balderas, M. Ortega-Munoz, J. Morales-Sanfrutos, F. Hernandez-Mateo, F. G. Calvo-Flores, J. A. Calvo-Asin, J. Isac-Garcia and F. Santoyo-Gonzalez, *Org. Lett.*, 2003, **5**, 1951.
60 Ch. W. Tornoe, C. Christensen and M. Meldal, *J. Org. Chem.*, 2002, **67**, 3057.
61 A. R. Katritzky, Y. Zhang and S. K. Singh, *Heterocycles*, 2003, **60**, 1225.
62 J. R. Bailey and N. H. Moore, *J. Am. Chem. Soc.*, 1917, **39** 279.
63 R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, 1963, **2**, 565.
64 O. Nuyken, G. Maier and K. Burger, *Makromol. Chem.*, 1988, **189**, 2245.
65 G. Maier, *Macromol. Chem. Phys.*, 1996, **197**, 3067.
66 K. Burger, L. Hennig, O. Zeika and A. Lux, *Heterocycles*, 2006, **67**, 443, and references therein.
67 G. Maier, C. Zech, B. Voit and H. Komber, *Macromol. Chem. Phys.*, 1998, **199**, 2655.
68 G. Maier, C. Zech, B. Voit and H. Komber, *Macromol. Symp.*, 2001, **163**, 75.
69 B. Voit, G. Maier, C. Zech, H. Komber, A. Scheel and C. Hawker, *PMSE [Prepr.]*, 2004, **91**, 258.
70 M. Smet, E. Schacht and W. Dehaen, *Angew. Chem.*, 2002, **114**, 4729.
71 G. van Wuytswinkel, B. Verheyde, F. Compernolle, S. Toppet and W. Dehaen, *J. Chem. Soc., Perkin Trans. 1*, 2000, 1337.
72 P. Wu, A. K. Feldman, A. K. Nugent, C. J. Hawker, A. Scheel, B. Voit, J. Pyun, J. M. J. Fréchet, K. B. Sharpless and V. V. Fokin, *Angew. Chem., Int. Ed.*, 2004, **43**, 3928.
73 K. E. Johnson, J. A. Lovinger, C. O. Parker and M. G. Baldwin, *J. Polym. Sci., Part B: Polym. Lett.*, 1966, **4**, 977.
74 B. S. Sumerlin, N. V. Tsarevsky, G. Louche, R. Y. Lee and K. Matyjaszewski, *Macromolecules*, 2005, **38**, 7540.
75 M. Malkoch, R. J. Thibault, E. Drockenmuller, M. Messerschmidt, B. Voit, T. P. Russell and C. J. Hawker, *J. Am. Chem. Soc.*, 2005, **127**, 14942.
76 N. V. Tsarevsky, B. S. Sumerlin and K. Matyjaszewski, *Macromolecules*, 2005, **38**, 3558.
77 J. A. Opsteen and J. C. M. van Hest, *Chem. Commun.*, 2005, 57.
78 J. W. Lee and B. K. Kim, *Bull. Korean Chem. Soc.*, 2005, **26**, 658.
79 J. W. Lee and B. K. Kim, *Synthesis*, 2006, **4**, 615.
80 J. W. Lee, B. K. Kim, H. J. Kim, S. C. Han, W. S. Shin and S. H. Jin, *Macromolecules*, 2006, **39**, 2418.
81 J. W. Lee, J. H. Kim, B. K. Kim, W. S. Shin and S. H. Jin, *Tetrahedron*, 2006, **62**, 894.
82 J. W. Lee, J. H. Kim and B.-K. Kim, *Tetrahedron Lett.*, 2006, **47**, 2683.
83 M. J. Joralemon, R. K. O'Reilly, J. B. Matson, A. K. Nugent, C. J. Hawker and K. L. Wooley, *Macromolecules*, 2005, **38** 5436.
84 M. Malkoch, K. Schleicher, E. Drockenmuller, C. J. Hawker, T. P. Russel, P. Wu and V. V. Fokin, *Macromolecules*, 2005, **38** 3663.
85 P. Wu, M. Malkoch, J. N. Hunt, R. Vestberg, E. Kaltgrad, M. G. Finn, V. V. Fokin, K. B. Sharpless and C. J. Hawker, *Chem. Commun.*, 2005, 5775.
86 J. L. Mynar, T.-L. Choi, M. Yoshida, V. Kim, C. J. Hawker and J. M. J. Fréchet, *Chem. Commun.*, 2005, 5169.
87 D. T. S. Rijkers, G. W. van Esse, R. Merkx, A. J. Brouwer, H. J. F. Jacobs, R. J. Pieters and R. M. J. Liskamp, *Chem. Commun.*, 2005, 4581.
88 J. A. F. Joosten, N. T. H. Tholen, F. Ait El Maate, A. J. Brouwer, G. W. van Esse, D. T. S. Rijkers, R. M. J. Liskamp and R. J. Pieters, *Eur. J. Org. Chem.*, 2005, 3182.
89 E. Fernandez-Megia, J. Correa, I. Rodríguez-Meizoco and R. Riguera, *Macromolecules*, 2006, **39**, 2113.
90 C. Ornelas, J. R. Aranzaes, E. Cloutet, S. Alves and D. Astruc, *Angew. Chem., Int. Ed.,* DOI: 10.1002/anie.200602858.
91 L. Perez, J. Garcia-Martinez, E. Diez-Barra, P. Atienzar, H. Garcia, J. Rodriguez-Lopez and F. Langa, *Chem.–Eur. J.*, 2006, **12**, 5149.
92 B. Helms, J. L. Mynar, C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2004, **126**, 15020.
93 M. J. Joralemon, R. K. O'Reilly, C. J. Hawker and K. Wooley, *J. Am. Chem. Soc.*, 2005, **127**, 16892.
94 A. Scheel, H. Komber and B. Voit, *Macromol. Rapid Commun.*, 2004, **25**, 1175.
95 M. Smet, K. Metten and W. Dehaen, *Collect. Czech. Chem. Commun.*, 2004, **69**, 1097.
96 A. Scheel, *Thermisch labile hochverzweigte Polycarbonate und Poly[1,2,3]triazolcarbonate*, PhD Thesis, Technische Universität Dresden, Verlag Dr. Hut, München, 2006.
97 V. van. Speybroeck, Y. Martele, M. Waroquier and E. J. Schacht, *J. Am. Chem. Soc.*, 2001, **123**, 10650.